POLARISATION DEPENDENCE OF MULTIPHOTON SPECTROSCOPY

A Thesis

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by

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To my Parents

Thank you

ABSTRACT

Group theoretical techniques are used to analyse the polarisation dependence of multiphoton processes. The analysis is sufficiently general to be applied to all point group symmetries and in a wide variety of physical situations. For two photon spectroscopy, a method is developed for extracting the maximum information available from polarisation studies. It is shown that measurements involving circular polarisations of the light beams are always required to determine all the parameters contributing to the intensities. Detailed results are given for the case of time reversal even interactions for electric dipole coupling. The analysis is applied to non resonant vibrational Raman scattering in the presence of degenerate electronic states. Existing selection rules are extended allowing a proof that symmetric and antisymmetric amplitude terms do not interfere. Complete tables of selection rules are given for both oriented and random scatterers. Non linear effects are also considered. Diagram techniques provide an efficient method for separating the geometrical factors which contribute to the hyper Raman scattering intensity. New symmetry restrictions are postulated for the four photon C.A.R.S. process. Handed effects are also considered and in particular natural and induced circular dichroism. Both the M.C.D. and E.C.D. spectra are shown to be isotropic or axially symmetric in certain point groups.

ACKNOWLEDGEMENTS

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CHAPTER ONE

INTRODUCTION

Group theory provides a powerful tool which has become indispensable in many branches of physics. In particular, solid state physics relies heavily on symmetry considerations (e.g. in the determination of selection rules) and also tensorial techniques (e.g. in crystal field theory). Recent advances in group theoretical methods have provided a more rigorous foundation for such applications (see N.A.T.O. ASIS vol 43 ed Donini 1979). We use such techniques to develop a formalism for studying the symmetry properties of spectroscopic processes. In particular we investigate the polarisation dependence of a variety of multiphoton effects. The scattering processes involved invite a comparison with many body perturbation theory, which has been applied to Raman scattering (e.g. McKenzie and Stedman (1978)). The Feynman diagrams may be interpreted group theoretically and this work has been generalised to finite groups by Stedman (1975). Such techniques have made possible a rigorous group theoretical analysis of scattering processes. Attention to branching and product multiplicities, phases, and time reversal symmetries allows new and more precise results to be obtained. Recently Butler (1981) has generated complete tables of 6J and 3JM symbols for all point groups. These allow detailed numerical results to be obtained. We use Butler's notation and phase conventions throughout this work.

In chapter two we consider the symmetry properties of a general two photon scattering process. It is possible to express the intensity as a product of two terms: a physical constant which embodies all the dependence on the interactions, and a geometrical factor which is purely a function of the polarisation vectors. Many authors have investigated the form of the geometrical factors. In two photon spectroscopy such work was pioneered by Inoue and Toyozawa (1965) and extended to the case of degenerate electronic ground states by Bader and Gold (1968). The work of these authors however is only relevant for real polarisation vectors i.e. linearly polarised radiation beams. Fröhlich et al (1970) showed that measurements involving circularly polarised light are necessary for a complete analysis of the absorption spectrum in O_h symmetry. We generalise this work to all point group symmetries filling a gap in the literature noted by Worlock (1972). We prove that measurements with circularly polarised light are always necessary to determine all the independent parameters contributing to the spectrum. More recently workers such as Birman and Berenson (1974), have used tensorial techniques to analyse the scattering tensors. However these authors do not include time reversal arguments in their general development. Doni et al (1974) and Denisov and Markarov (1972) consider time reversal symmetries, however the former give detailed results only for the cubic groups while the latter assume singlet electronic ground states. Our analysis generalises the results of these authors.

We expand the geometrical and physical factors which contribute to the intensity in terms of three bases. Two of these, the cartesian and spherical bases will be familiar to those who work with scattering tensors or in crystal field theory. The third basis is described in terms of irreducible representations of group-subgroup chains. This basis proves particularly useful for determining selection rules. We determine the relationships between these bases and in so doing hope to reconcile the different approaches to symmetry in solid state physics. A method is developed for deducing the physical constants from sets of independent experimental measurements and so enabling the extraction of the maximum information available from polarisation studies.

In chapter three these techniques are applied to the case of non resonant vibrational Raman scattering. This process has been studied by many authors since the time of Placzek (1934). Generally an adiabatic approach has been used but we prefer to work with third order perturbation theory (e.g. Loudon 1963). This provides a more general method that does not require any adiabatic approximations. Johnson and Peticolas (1976) compare the two methods in their review article. We generalise the results of Loudon to include degenerate electron ground states and in so doing derive a selection rule which is consistent with that of Child (1963). Our rule, which includes multiplicity labels, is somewhat stronger and

this allows the proof that symmetric and antisymmetric amplitude terms will not interfere in the non resonant case. Thus, although antisymmetric terms are permitted in the amplitude for degenerate ground states, the intensity remains symmetric. This explains the result of Kiel et al who searched for but did not observe antisymmetric terms in the intensity. Barron and Nørby Svendson (1980) use time reversal considerations to develop a selection rule equivalent to that of Child while workers such as Konigstein et al (1976) offer an inequivalent rule. We discuss the problems encountered by these authors later. We provide complete tables of selection rules for all electronic ground states and phonon modes for both oriented and random scatterers in all point groups. The existence of degenerate electronic ground states can allow extra terms in the intensity. We find that our analysis can account for the otherwise unexplained observations of Johnstone et al (1980). These authors found that a phonon mode was excited by polarisations of the radiation beams that were not predicted by the familiar Loudon selection rules.

We show how the analysis can be extended to non linear processes in chapter four. We investigate the polarisation dependence of the three photon hyper Raman process. Diagram techniques provide a concise method for describing the different contributions to the intensity. We express the intensity in terms of scalar products of polarisation vectors and obtain a generalisation of the result of Andrews

et al (1978). Our analysis allows an unambiguous separation of the geometrical factors and also permits the inclusion of time reversal odd interactions. We give selection rules for hyper Raman scattering in random scatterers for all electronic ground states and in all point groups. The four photon C.A.R.S. effect is also examined. For the non resonant case we discuss symmetries analogous to those which applied for Raman scattering. This is possible as the numbers of incident and scattered photons are equal.

In chapter five handed effects are considered. In particular we examine natural and induced circular dichroism. In the standard works (for example Buckingham and Stephens (1966)) little use is made of symmetry considerations. More recently tensorial techniques have been used to study M.C.D. Dobosh et al (1973) use these methods to recover standard results for O_h symmetry. Manson et al (1977) use similar techniques to prove that the M.C.D. spectrum is isotropic in cubic crystals. The restrictions imposed by symmetry can be generalised to all point groups by our methods and this gives rise to several new results. We show that natural circular dichroism may be expected in some achiral point groups. For M.C.D. we give a simple proof of Manson's result and also show that the spectrum will be axially symmetric for some symmetries. Similar results also apply to E.C.D. We tabulate the polarisation dependence of both effects for all point group symmetries. These results

are all open to easy experimental verification. We indicate how these methods could be applied to higher order effects e.g. Raman optical activity (Barron and Buckingham (1975)).

These examples demonstrate the versatility of our approach to symmetry in spectroscopy. The analysis is sufficiently general to be useful in a variety of physical situations and can be applied to all symmetries. It is clear that much information is available from the use of these techniques.

CHAPTER TWO

TWO PHOTON SPECTROSCOPY

Two photon effects play a large and important role in the field of optical spectroscopy. Such processes include two photon absorption, Rayleigh and Raman scattering. We are concerned primarily with the polarisation dependence of these effects. Much information about the electronic states, photon modes and the symmetry of the scatterer can be obtained by varying the polarisations of the radiation beams with respect to one another and the crystallographic axes. Much work has been done in this area although many workers limit their analyses to the case of non degenerate electronic states or to linear polarisations of the radiation beams.

The theory of Raman scattering for non degenerate electronic states has been well known since the time of Placzek(1934). Selection rules for this case have been tabulated by many authors (Loudon (1964), Ovander(1969), McClain (1971)). The extension of this work to the case of degenerate electronic ground states has been considered by workers such as Child and Longuet-Higgins (1961), Child (1962), Konigstein (1975), Parameswaran et al (1977) and Barron and Nørby Svendson (1980). We consider this situation in detail for the case of non resonant vibrational Raman scattering in chapter three.

Work in the related field of two photon absorption was pioneered by Inoue and Toyozawa (1965). Their work was

extended by Bader and Gold (1968) to include transitions from all possible ground states.

The importance of measurements involving circularly polarised light has been recognised since the work of Placzek (1934) for randomly orientated scatterers. More recently authors such as Fröhlich (1970) and Bayer and Schaak (1970) have shown that circular polarisations are necessary to determine unambiguously the symmetry contributions of a spectrum in O_h symmetry. The extension of this work to other symmetries has not been done as noted by Worlock (1972).

In this chapter we present a generalised formalism which can be applied to all two photon processes. The analysis is based on group theoretic considerations and the attention to phases, multiplicities and so on means that the results can be applied directly to any group from C_1 (i.e. no symmetry) to R_3 (full rotational symmetry). We deduce the number of independent spectra which contribute for particular physical situations and develop a method for extracting this information from experimental results. We show that measurements with circularly polarised light are always necessary to determine all the independent scattering parameters. For the case of electric dipole coupling in the absence of external fields we give detailed results of the above analysis for all point groups.

2.1 INTERACTION OF RADIATION WITH MATTER

The interaction of radiation with matter is studied in many standard texts for example, Messiah (1961), Loudon (1973). We take the Hamiltonian for the interaction as having the form

$$\mathcal{H} = \frac{-q}{m} \underline{A}.\underline{p} \tag{2.1}$$

where $\underline{A}(\underline{r},t)$ is the vector potential of the radiation in a coulomb gauge and $\underline{p}$ the electron momentum. The vector potential can be expressed in a quantum-mechanical form as

$$\underline{A} = \sum_{\underline{k}j} c(\underline{k}) [\underline{e}_{\underline{k}j} \hat{a}_{\underline{k}j} \exp i (\underline{k}.\underline{r}-\omega t) + \underline{e}^*_{\underline{k}j} \hat{a}^\dagger_{\underline{k}j} \exp -i(\underline{k}.\underline{r}-\omega t)] \tag{2.2}$$

$\hat{a}_{\underline{k}j}$ and $\hat{a}^\dagger_{\underline{k}j}$ are the annihilation and creation operators respectively for a photon with wavevector $\underline{k}$, polarisation j, and unit polarisation vector $\underline{e}_{\underline{k}j}$. Note that the destruction (or absorption) of a photon will be associated with the term $\underline{e}_{\underline{k}j} \hat{a}_{\underline{k}j}$, while the creation (or scattering) of a photon will arise from the term $\underline{e}^*_{\underline{k}j} \hat{a}^\dagger_{\underline{k}j}$. Many authors assume linear polarisations and do not distinguish $\underline{e}$ and $\underline{e}^*$.

We can expand the time independent part of the vector potential as

$$\underline{A}(\underline{r}) = \sum_{\underline{k}j} c(\underline{k}) [\underline{e}_{\underline{k}j} \hat{a}_{\underline{k}j}(1 + i\underline{k}.\underline{r} + \ldots) + \text{h.c.}] \tag{2.3}$$

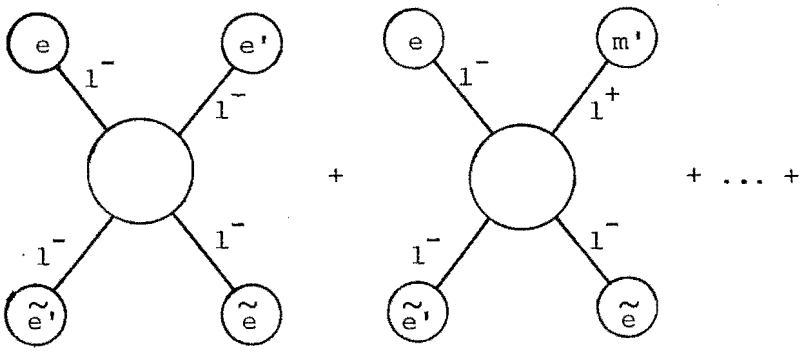
The interaction Hamiltonian will then have the form

$$\mathcal{H}(\underline{r}) \propto \sum_{\underline{k}j} \hat{a}_{\underline{k}j} (\underline{e}_{\underline{k}j}.\underline{p} + i(\underline{k}.\underline{r})(\underline{e}_{\underline{k}j}.\underline{p}) + \ldots) + \text{h.c.} \tag{2.4}$$

The first term corresponds to the electric dipole interaction while the second gives rise to the magnetic dipole and electric quadrupole couplings (see appendix A1).

The amplitude for a two photon experiment will require two such interactions and will be quadratic in $\underline{e}$. The intensity will therefore be a quartic in the polarisation vectors. We let $I(\underline{e}\ \underline{e}')$ denote the intensity of the Raman spectrum for incident polarisation $\underline{e}$ and scattered polarisation $\underline{e}'^*$, or the absorption spectrum for two photons with polarisation $\underline{e},\underline{e}'$. We can represent $I(\underline{e}\ \underline{e}')$ as in the diagram

$I(\underline{e}\ \underline{e}') =$



$+ \ldots +$

where the first term represents all electric dipole interactions while the second term represents one of four interference terms between electric and magnetic dipole couplings.

The polarisation vectors $\underline{e}$ are polar vectors transforming as $j = 1^-$ of the rotation group. We define the conjugate polarisation for component ρ as

$$\tilde{e}_\rho = \begin{pmatrix} 1^- \\ \rho \end{pmatrix} e^*_{\rho *} \qquad (2.5)$$

where $\begin{pmatrix} 1^- \\ \rho \end{pmatrix}$ is a 2JM factor. (With this definition, linearly polarised light satisfies $\tilde{\underline{e}} = \underline{e}$ in any basis). Generally we consider $\underline{e}$ in terms of a cartesian basis in which case equation 2.5 reduces to $\tilde{\underline{e}} = \underline{e}^*$. The magnetic dipole moment $\underline{m}$ is an axial vector given by

$$\underline{m} = i\, \underline{e} \times \underline{k} \tag{2.6}$$

In appendix A1 we choose a phase convention for right (R) and left (L) circularly polarised light and show that

$$\begin{aligned} \tilde{\underline{e}}_R &= \underline{e}_L \\ \tilde{\underline{m}}_R &= -\underline{m}_L \end{aligned} \tag{2.7}$$

while for linear light

$$\begin{aligned} \tilde{\underline{e}} &= \underline{e} \\ \tilde{\underline{m}} &= -\underline{m} \end{aligned} \tag{2.8}$$

2.2 SYMMETRIES OF THE INTENSITY

We find it useful to divide the intensity into parts which have specific symmetry properties. These symmetries involve interchanging $\underline{e}$ and $\underline{e}'$ and considering the effect of the transformation $\underline{e} \to \tilde{\underline{e}}$, $\underline{e}' \to \tilde{\underline{e}}'$.

We write the intensity as the sum of four terms

$$I(\underline{e}\ \underline{e}') = \sum_{\eta\varepsilon} I^{\eta\varepsilon}(\underline{e}\ \underline{e}') \tag{2.9}$$

where η,ε take the values $\pm$ 1 and are defined by the symmetries

$$I^{\eta\varepsilon}(\underline{e}\ \underline{e}') = \varepsilon\ I^{\eta\varepsilon}(\underline{e}'\underline{e}) \tag{2.10}$$

$$I^{\eta\varepsilon}(\underline{e}\ \underline{e}') = \eta\ I^{\eta\varepsilon}(\tilde{\underline{e}}\ \tilde{\underline{e}}') \tag{2.11}$$

Scattering mechanisms obeying equation 2.10 are referred to as symmetric or antisymmetric scatterers as $\varepsilon = \pm 1$. We show in Chapter 3 that the non resonant phonon Raman effect is an example of a symmetric scattering process where there is no contribution from $\varepsilon = -1$ terms. This means that the incident and scattered polarisations may be exchanged without any change in the intensity.

The second symmetry is a conjugation symmetry and is closely linked with the time reversal properties of the scattering process. Mechanisms or processes which involve only a contribution from $\eta = +1$ terms are referred to as real scatterers. Electric dipole coupling in the absence of external fields is an example of a real scattering process. In general processes are 'complex' that is they have contributions from terms with both $\eta = +1$ and $\eta = -1$.

Terms with $\eta = -1$ give rise to handed effects. As an example we consider the Raman circular intensity differential (Barron and Buckingham (1975), Barron (1979)) in which the intensity difference for right or left circularly polarised incident light is measured. If $\underline{e}'$ is a linear component of the scattered light i.e. $\tilde{\underline{e}}' = \underline{e}'$ then we have

$$I(\underline{e}_R\ \underline{e}') = \sum_{\varepsilon} I^{+\varepsilon}(\underline{e}_R\ \underline{e}') + I^{-\varepsilon}(\underline{e}_R\ \underline{e}')$$

$$= \sum_{\varepsilon} I^{+\varepsilon}(\underline{e}_L\ \underline{e}') - I^{-\varepsilon}(\underline{e}_L\ \underline{e}')$$

where we have used (2.7) and (2.11). It is clear that the intensities for right and left circularly polarised incident light will be the same if $I^{-\varepsilon}(\underline{e}\ \underline{e}') = 0$. We therefore require a contribution from the $\eta = -1$ terms in order to observe these effects. Such terms can arise from magnetic dipole coupling or from including time reversal odd interactions such as external magnetic fields.

We now analyse the properties of the intensity for the different physical situations corresponding to these symmetries.

2.3 BASES FOR EXPANDING THE INTENSITY

We have indicated that for two photon effects the intensity is a quartic in the polarisation vectors $\underline{e}$, $\underline{e}'$. It is possible to split the intensity into two factors. One, $F_\alpha(\underline{e}\ \underline{e}')$, contains the geometrical information i.e. the scattering angle, polarisers, analysers etc and is purely a function of the polarisation vectors. The other, $C_\alpha(\Omega)$, is independent of the polarisation vectors and is a physical constant containing all the dependence on the interactions involved in the scattering. It will therefore be dependent on electronic and phonon symmetries and photon and phonon frequencies (Ω).

We can write the intensity in terms of these factors as

$$I(\underline{e}\ \underline{e}') = \sum_{\alpha} F_{\alpha}(\underline{e}\ \underline{e}')\ c_{\alpha}(\Omega) \qquad (2.12)$$

We consider the expansion in three different bases: a cartesian basis, a spherical basis and a point group basis. The cartesian basis has been widely used in the past for describing the properties of the Raman scattering tensor (Loudon 1964) and also in elasticity theory. The spherical basis will be familiar to workers in crystal field theory as many of their parameters are described in terms of spherical harmonics. We find the point group basis which is described in terms of irreducible representations and their multiplicities particularly useful when it comes to deriving selection rules. By describing all three bases and the relationships between them we aim to reconcile the different approaches of traditional solid state theory and give a general account of symmetry considerations.

We perform symmetrisations which split the factors into terms with definite values for η and ε so that we have

$$I(\underline{e}\ \underline{e}') = \sum_{\eta\varepsilon\alpha} F_{\alpha}^{\eta\varepsilon}(\underline{e}\ \underline{e}')\ c_{\alpha}^{\eta\varepsilon}(\Omega) \qquad (2.13)$$

We deduce the number of terms expected in the sum for a particular physical situation (i.e. value of η,ε) in different point group symmetries. The factors $F_{\alpha}^{++}(\underline{e}\ \underline{e}')$ are tabulated for electric dipole coupling in each basis for all point groups.

(a) Cartesian Basis

Many tables of scattering amplitudes are given in terms of a cartesian basis. The expression for the intensity may be written as

$$I(\underline{e}\ \underline{e}') = \sum_{\rho\rho'\sigma\sigma'} F_{\rho\rho'\sigma\sigma'}(\underline{e}\ \underline{e}')\ c_{\rho\rho'\sigma\sigma'}(\Omega) \qquad (2.14)$$

where $F_{\rho\rho'\sigma\sigma'}(\underline{e}\ \underline{e}')$ is a quartic in the polarisation vectors

$$F_{\rho\rho'\sigma\sigma'}(\underline{e}\ \underline{e}') = e_\rho e'_\rho\ e^*_\sigma e'^*_\sigma \qquad (2.15)$$

In general there are $3^4 = 81$ choices of labels $\rho,\rho',\sigma,\sigma'$, $= x,y,z$ i.e. 81 independent spectra $c_{\rho\rho'\sigma\sigma'}$.

We can take a symmetrised combination of the polarisation vectors

$$[\underline{e}\ \underline{e}']^{\eta\varepsilon}_{\rho\rho'\sigma\sigma'} = \frac{\theta_\eta}{k}\,[e_\rho e'_\rho\ e^*_\sigma e'^*_\sigma + \varepsilon e_\rho, e'_\rho\ e^*_\sigma, e'^*_\sigma$$

$$+ \eta(e_\sigma e'_\sigma\ e^*_\rho e'^*_\rho + \varepsilon e_\sigma, e'_\sigma e^*_\rho, e'^*_\rho)] \qquad (2.16)$$

where $\theta_\eta = 1,(i)$ as $\eta = 1(-1)$. The transformation is orthonormal if we include the factor $\frac{1}{k}$, where

$k = 4$ if all indices $\rho,\rho',\sigma,\sigma'$, are equal

$k = 2\sqrt{2}$ if indices are equal in pairs

$k = 2$ otherwise (2.17)

The intensity now becomes

$$I(\underline{e}\ \underline{e}') = \sum_{\rho\rho'\sigma\sigma'\eta\varepsilon} F^{\eta\varepsilon}_{\rho\rho',\sigma\sigma'}(\underline{e}\ \underline{e}')\ c^{\eta\varepsilon}_{\rho\rho',\sigma\sigma'}(\Omega) \qquad (2.18)$$

where

$$F^{\eta\varepsilon}_{\rho\rho',\sigma\sigma'}(\underline{e}\ \underline{e}') = [\underline{e}\ \underline{e}']^{\eta\varepsilon}_{\rho\rho',\sigma\sigma'} \qquad (2.19)$$

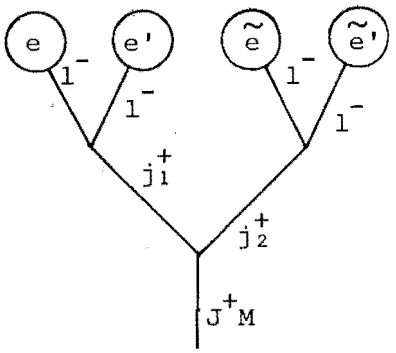
The sum over $\rho\rho'\sigma\sigma'$ is now only over 27 primitive values (see table 4). For example if $\rho\rho'\sigma\sigma'$ is included we do not require $\rho'\rho\sigma'\sigma$, $\sigma\sigma'\rho\rho'$, $\sigma'\sigma\rho'\rho$. The sum over η,ε makes this number up to 81 and for a particular situation one need only include the appropriate values of η and ε.

Point group symmetry further reduces the number of independent factors $F^{\eta\varepsilon}_{\rho\rho',\sigma\sigma'}(\underline{e}\ \underline{e}')$. The symmetry creates linear relationships between the cartesian quartics $\rho\rho'\sigma\sigma'$ and these can be used to form orthonormal symmetrised combinations of the geometrical factors. These are not simply a group average and they need to be constructed independently for each group. The independent symmetrised factors $F^{++}_{\rho\rho',\sigma\sigma'}(\underline{e}\ \underline{e}')$ for the case of real symmetric scatterers can be found in table 8 for all point groups.

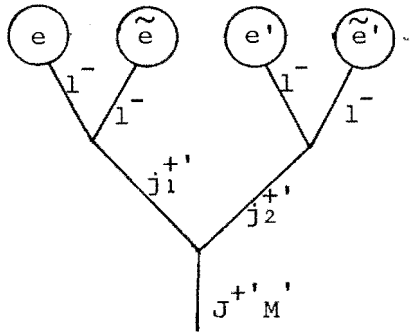
(b) Spherical Basis

The polarisation vectors transform as $J = 1^-$ of the full rotation group O_3. For electric dipole coupling we can couple two vectors from the quartic $e_\rho e'_{\rho'} e^*_\sigma e'^*_{\sigma'}$ to give components of angular momentum $j_1 = 0^+, 1^+, 2^+$ and the remaining two likewise to $j_2 = 0^+, 1^+, 2^+$. j_1 and j_2 can then

be coupled to give an angular momentum J with component M where J can take values from $0^+ \rightarrow 4^+$. A standard coupling is to couple incident and scattered vectors i.e. $\underline{e}$ with $\underline{e}'$ to give j_1 and similarly with their conjugates to give j_2. Alternatively we can couple each vector with its conjugate i.e. $\underline{e}$ with $\underline{\tilde{e}}$ and $\underline{e}'$ with $\underline{\tilde{e}}'$ (see diagram.)

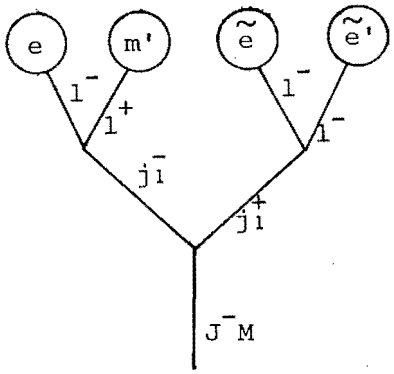


Standard coupling



Alternative coupling

The same procedure can be carried out if we have a magnetic dipole term included. However $\underline{m} = i\ \underline{e} \times \underline{k}$ transforms as $j = 1^+$. The diagrams then include a mixture of polar and axial vectors.



electric dipole-magnetic dipole coupling

All of the following can be applied to this case if one bears in mind that some of the angular momenta, J now transform as polar vectors. This is particularly important

when reducing onto a point group as groups containing reflections or inversions have different transformation properties when branching from J^+ and J^-. For the rest of this section we assume electric dipole coupling.

We can transform from the cartesian to the spherical basis (standard coupling) by means of a unitary transformation $T^{j_1 j_2 JM}_{\rho\rho'\sigma\sigma'}$

$$e_\rho e'_\rho \; e^*_\sigma e'^*_\sigma = \sum_{j_1 j_2 JM} T^{j_1 j_2 JM}_{\rho\rho'\sigma\sigma'} \; [\underline{e}\;\underline{e}']_{j_1 j_2 JM} \tag{2.20}$$

where

$$T^{j_1 j_2 JM}_{\rho\rho'\sigma\sigma'} = \sum_{\substack{mm'nn' \\ m_1 m_2}} \langle 1^- m | 1^- \rho \rangle \langle 1^- m' | 1^- \rho' \rangle \langle 1^- n | 1^- \sigma \rangle \langle 1^- n' | 1^- \sigma' \rangle$$
$$\hat{j}_1 \hat{j}_2 \hat{J} \begin{pmatrix} 1^- & 1^- & j_1^+ \\ m & m' & -m_1 \end{pmatrix} \begin{pmatrix} 1^- & 1^- & j_2^+ \\ n & n' & -m_2 \end{pmatrix} \begin{pmatrix} j_1^+ & j_2^+ & J^+ \\ m_1 & m_2 & -M \end{pmatrix} \tag{2.21}$$

where $\hat{J} = (2J + 1)^{\frac{1}{2}}$. The first terms are transformation coefficients between cartesian and spherical bases and throughout we use a contrastandard transformation defined by

$$|1^- \pm 1\rangle \equiv \frac{1}{\sqrt{2}} (y \mp ix)$$

$$|1^- 0\rangle \equiv iz \tag{2.22}$$

From the definition equation 2.21 we can use the symmetry properties of the 3JM symbols to show that

$$T^{j_1 j_2 JM}_{\rho\rho'\sigma\sigma'} = (T^{j_1 j_2 J-M}_{\rho\rho'\sigma\sigma'})^* \ (-)^{J-M}$$

$$= (-)^{j_1+j_2} \ T^{j_1 j_2 JM}_{\rho'\rho\sigma'\sigma}$$

$$= (-)^{j_1+j_2+J} \ T^{j_2 j_1 JM}_{\sigma\sigma'\rho\rho'} \qquad (2.23)$$

The symmetrised cartesian factors can be expressed in terms of the spherical basis as

$$[\underline{e}\ \underline{e}']^{\eta\varepsilon}_{\rho\rho'\sigma\sigma'} = \frac{1}{k}(1 + \varepsilon(-)^{j_1+j_2})\{T^{j_1 j_2 JM}_{\rho\rho'\sigma\sigma'}$$

$$+ \eta(-)^{j_1+j_2+J} \ T^{j_2 j_1 JM}_{\rho\rho'\sigma\sigma'}\}[\underline{e}\ \underline{e}']_{j_1 j_2 JM} \qquad (2.24)$$

We therefore define new transformation factors

$$T^{j_1 j_2 JM}_{\rho\rho'\sigma\sigma'\eta\varepsilon} = \frac{1}{2kg} (1 + \varepsilon(-)^{j_1+j_2})\{T^{j_1 j_2 JM}_{\rho\rho'\sigma\sigma'}$$

$$+ \eta(-)^{j_1+j_2+J} \ T^{j_2 j_1 JM}_{\rho\rho'\sigma\sigma'}\} \qquad (2.25)$$

where $g = \sqrt{2}$ if $j_1 \neq j_2$ and $g = 2$ otherwise. These factors can now be made real using the first part of equation 2.23. Abbreviating $T^{j_1 j_2 JM}_{\rho\rho'\sigma\sigma'\eta\varepsilon}$ to T^{JM} we define

$$T^{JM\theta} = \frac{1}{\sqrt{2}} (T^{JM} \ (-)^{J-M} + T^{J\ -M}) \quad m > 0 \quad \theta = +$$

$$= \frac{-i}{\sqrt{2}} (T^{JM} \ (-)^{J-M} - T^{J\ -M}) \quad m > 0 \quad \theta = -$$

$$= T^{JM} \qquad m = 0 \qquad (2.26)$$

We now have a fully symmetrised transformation

$$[\underline{e}\ \underline{e}']^{\eta\varepsilon}_{\rho\rho'\sigma\sigma'} = \sum_{j_1 j_2 JM\theta} T^{j_1 j_2 JM\theta}_{\rho\rho'\sigma\sigma'\eta\varepsilon}\ [\underline{e}\ \underline{e}']^{\eta\varepsilon}_{j_1 j_2 JM\theta} \qquad (2.27)$$

We indentify $F^{\eta\varepsilon}_{j_1 j_2 JM}(\underline{e}\ \underline{e}')$ with the coupled polarisation vectors in equation 2.27 and so have

$$I(\underline{e}\ \underline{e}') = \sum_{j_1 j_2 JM\theta\eta\varepsilon} F^{\eta\varepsilon}_{j_1 j_2 JM\theta}(\underline{e}\ \underline{e}')\ c^{\eta\varepsilon}_{j_1 j_2 JM\theta}(\Omega) \qquad (2.28)$$

where

$$F^{\eta\varepsilon}_{j_1 j_2 JM}(\underline{e}\ \underline{e}') = \sum_{\rho\rho'\sigma\sigma'} (T^{j_1 j_2 JM\theta}_{\rho\rho'\sigma\sigma'\eta\varepsilon})^{-1}\ [\underline{e}\ \underline{e}']^{\eta\varepsilon}_{\rho\rho'\sigma\sigma'} \qquad (2.29)$$

The transformation factors $T^{j_1 j_2 JM\theta}_{\rho\rho'\sigma\sigma'++}$ can be found in table 5 while the geometrical factors $F^{++}_{j_1 j_2 JM\theta}(\underline{e}\ \underline{e}')$ and their inverses are given in tables 6 and 7 for an independent set of $\underline{e},\underline{e}'$.

We see from equation 2.25 that for the factors T and F to be non zero we must have that

$$\varepsilon(-)^{j_1+j_2} = +1 \qquad (2.30)$$

The values of the labels $j_1 j_2 J$ which contribute for particular η and ε are given in figure 2.1.

The number of terms which contribute to the sum (equation 2.28) for particular values of η and ε is easily calculated in this basis and these are given in figure 2.1 also. For the more detailed tables we confine our attention to the 27 x 27 block associated with real symmetric scatterers.

j_1+j_2 / $\varepsilon\eta$	even		odd	
++	✓			
+-		✓		
-+			✓	
--				✓
values of $j_1 j_2 J$	000 (+)022 110 222 224 220 112	(-)022 111 221 223	(+)011 (+)123 (+)121 (-)122	(-)011 (-)123 (-)121 (+)122
no of terms	27	18	18	18

Figure 2.1: Terms $j_1 j_2 JM\theta$ which contribute for particular $\eta\varepsilon$ in the standard coupling. The sign in parenthesis is $\eta\varepsilon(-)^J$ which indicates symmetric or antisymmetric combinations of $j_1 j_2$ (eqn 2.25). For the alternative coupling interchange η, ε.

The effect of point group symmetry can be readily seen in this basis . Invariance under point group operations means that only those values of JM (or combinations of them) which

branch to the identity representation of the point group will contribute. These combinations can be found in Butler (1981) and will always involve the symmetrisations of equation (2.26). For the octahedral group we require the further symmetrisation for J = 4 terms

$$4c = \sqrt{\frac{7}{12}}\, 40 + \sqrt{\frac{5}{12}}\, 44_+ \quad . \tag{2.31}$$

These invariant combinations of JM terms are familiar in crystal field theory. In table 3 we list those values of $j_1 j_2 JM\theta$ which will contribute for each point group. Tables 5-7 can be simplified for a given point group symmetry by considering only the subset of $j_1 j_2 JM\theta$ which are applicable. See section 2.6 for examples.

(c) Point Group Basis

The sum in equation 2.12 can also be usefully expanded in terms of a point group basis. This basis is particularly convenient in problems where we wish to deduce selection rules for scattering off electron levels or producing phonons which transform as a particular representation of the point group (see chapter 3).

As for the spherical basis we first couple the polarisation vectors to j_1 and j_2 of SO_3. We then reduce these onto a point group. The transformation from cartesian labels to point group labels is

$$e_\rho e'_{\rho'} e^*_\sigma e'^*_{\sigma'} = \sum_{\substack{\mu n r \\ \mu' n' r'}} [\underline{e}\ \underline{e}']_{\mu n r}\ [\underline{e}\ \underline{e}']^*_{\mu' n' r'} \langle \mu n r | \bar{1}\rho, \bar{1}\rho' \rangle \langle \mu' n' r' | \bar{1}\sigma, \bar{1}\sigma' \rangle^* \tag{2.32}$$

where we define 'reducible' coupling coefficients

$$\langle \mu n r | 1^- \rho, 1^- \rho' \rangle = \sum_{mm'JM} \langle 1^- m | 1^- \rho \rangle \langle \bar{1} m' | 1^- \rho' \rangle \langle J^+ M | 1^- m, 1^- m' \rangle \langle \mu n r | J^+ M \rangle \qquad (2.33)$$

We also define a 'reducible 3JM'

$$\begin{pmatrix} 1 & 1 & \mu^* \\ \rho & \rho' & n^* \end{pmatrix} r = |\mu|^{-\frac{1}{2}} \begin{pmatrix} \mu \\ n \end{pmatrix} \langle \mu n r | 1\rho, 1\rho' \rangle \qquad (2.34)$$

We tabulate the coupling coefficients (equation 2.33) in table 2. The multiplicity labels r, r' distinguish repetitions of μ in the product $[1^- \otimes 1^-]$. They include the J label and are defined by a group subgroup chain e.g. $|J\lambda\mu\nu\tau\rangle$ where each label is an irrep label for a particular group in the chain. The multiplicity label is associated with groups higher in the chain i.e. $r \equiv J\lambda$ while the partner label is associated with lower groups i.e. $n \equiv \nu\tau$. Our choices of r are noted in table 2.

If the scatterer has a particular point group symmetry we can average over the operations of the group. Equation (2.32) becomes

$$\overline{e_\rho e'_{\rho'} e^*_\sigma e'^*_{\sigma'}} = \frac{1}{|g|} \sum_R \sum [\underline{e}\ \underline{e}']_{\mu n r} [\underline{e}\ \underline{e}']^*_{\mu' n' r'} \mu^-_{nn}(R) \mu^{*-}_{\bar{n}' n'}(R) \langle \mu n r | 1\rho, 1\rho' \rangle \langle \mu' n' r' | 1\sigma, 1\sigma' \rangle^* \qquad (2.35)$$

where $\mu^-_{nn}(R)$ is a matrix element for the group operation R,

$|g|$ is the order of the group, and there is a sum over repeated indices. The great orthogonality theorem can then be used to show that $\mu = \mu'$, $n = n'$ i.e.

$$e_\rho e'_{\rho'} e^*_\sigma e'^*_{\sigma'} = \sum_{\mu r r' n \bar{n}} |\mu|^{-1} [\underline{e}\ \underline{e}']_{\mu r \bar{n}} [\underline{e}\ \underline{e}']^*_{\mu r' \bar{n}} \langle \mu n r | 1\rho, 1\rho' \rangle \langle \mu n r' | 1\sigma, 1\sigma' \rangle^*$$

We define

$$T^{\mu r r'}_{\rho\rho'\sigma\sigma'} = \sum_n |\mu|^{-\frac{1}{2}} \langle \mu n r | 1\rho, 1\rho' \rangle \langle \mu n r' | 1\sigma, 1\sigma' \rangle^*$$

$$= \sum_n \binom{\mu}{n} |\mu|^{\frac{1}{2}} \begin{pmatrix} 1 & 1 & \mu^* \\ \rho & \rho' & n^* \end{pmatrix} r \begin{pmatrix} 1 & 1 & \mu \\ \sigma & \sigma' & n \end{pmatrix} r' \ \varepsilon^\mu_{r'} \qquad (2.36)$$

which is the unitary transformation between the cartesian and point group bases. The phases $\varepsilon^\mu_r = \pm 1$ come from the complex conjugation of the 3JM factors (see appendix A2), and their values are given in table 2. From its definition and the complex conjugation properties of the 3JM factors we see that T obeys the symmetries

$$T^{\mu r r'}_{\rho\rho'\sigma\sigma'} = T^{\mu^* r' r}_{\sigma\sigma'\rho\rho'} \ \varepsilon^\mu_r \ \varepsilon^\mu_{r'}$$

$$= \{11\mu r\}\{11\mu r'\} \ T^{\mu r r'}_{\rho'\rho\sigma'\sigma}$$

$$= (T^{\mu^* r r'}_{\rho\rho'\sigma\sigma'})^* \ \varepsilon^\mu_r \ \varepsilon^\mu_{r'} \qquad (2.37)$$

where $\{11\mu r\}$ is the 3J phase associated with reordering the columns of the 3JM factor. As in the case of the

spherical basis we wish to take combinations of $T^{\mu rr'}_{\rho\rho'\sigma\sigma'}$ to give real factors with definite values for η,ε. Equations (2.16 and 2.37) prompt the definition of new factors

$$T^{\mu rr'\eta\varepsilon\xi}_{\rho\rho'\sigma\sigma'} = \frac{\theta}{2kg'}\,(1 + \varepsilon\{11\mu r\}\{11\mu r'\})\{(T^{\mu rr'}_{\rho\rho'\sigma\sigma'} + \alpha T^{\mu^* r'r}_{\rho\rho'\sigma\sigma'}) + \xi(T^{\mu^* rr'}_{\rho\rho'\sigma\sigma'} + \alpha\, T^{\mu r'r}_{\rho\rho'\sigma\sigma'})\} \tag{2.38}$$

where $\alpha = \varepsilon^{\mu}_{r}\varepsilon^{\mu}_{r'}\eta$. The second part of the term is the complex conjugate of the first so the factors are real if $\theta = 1(i)$ as $\varepsilon^{\mu}_{r}\varepsilon^{\mu}_{r'}\xi = \pm 1$. The transformation is unitary if

$$\begin{aligned} g' &= 4 && \text{for } \mu = \mu^* \text{ and } r = r' \\ &= 2\sqrt{2} && \text{for } \mu = \mu^* \text{ or } r = r' \\ &= 2 && \text{for } \mu \neq \mu^* \text{ and } r \neq r' \end{aligned}$$

We now have that

$$[\underline{e}\ \underline{e}']^{\eta\varepsilon}_{\rho\rho'\sigma\sigma'} = \sum_{\mu rr'\xi} T^{\mu rr'\xi}_{\rho\rho'\sigma\sigma'\eta\varepsilon}\ [\underline{e}\ \underline{e}']^{\eta\varepsilon}_{\mu rr'\xi} \tag{2.39}$$

where the sum is taken only over values of r,r' such that $r' \geqslant r$ and only one of μ,μ^* if $\mu \neq \mu^*$. The expression for the intensity now becomes

$$I(\underline{e}\ \underline{e}') = \sum_{\eta\varepsilon\mu rr'\xi} F^{\eta\varepsilon}_{\mu rr'\xi}\ (\underline{e}\ \underline{e}')\ c^{\eta\varepsilon}_{\mu rr'\xi}(\Omega) \tag{2.40}$$

where the geometrical factors F(ee') are once again associated with the coupled polarisation vectors

$$F^{\eta\varepsilon}_{\mu rr'\xi}(\underline{e}\ \underline{e}') \equiv [\underline{e}\ \underline{e}']^{\eta\varepsilon}_{\mu rr'\xi} = \sum_{\rho\rho'\sigma\sigma'} \left(T^{\mu rr'\xi}_{\rho\rho'\sigma\sigma'\eta\varepsilon}\right)^{-1} [\underline{e}\ \underline{e}']^{\eta\varepsilon}_{\rho\rho'\sigma\sigma'} \tag{2.41}$$

The transformation coefficients T are given in table 8 and the geometrical factors F($\underline{e}$ $\underline{e}'$) and their inverses can be found in tables 9 and 10 for each point group.

From equation 2.38 we see that the factors T and F($\underline{e}$ $\underline{e}'$) are non zero only if

$$\{11\mu r\}\{11\mu r'\} = \varepsilon \tag{2.42}$$

we also note the restrictions that

$$\mu = \mu^* \text{ and } r = r' \Rightarrow \eta = +1,\ \xi = +1$$

$$\mu = \mu^* \text{ and } r \neq r' \Rightarrow \xi = +1$$

$$\mu \neq \mu^* \text{ and } r = r' \Rightarrow \eta\xi = +1 \tag{2.43}$$

We can use these restrictions to count the number of terms which will occur in the sum equation 2.40. If n^{λ}_{μ} is the number of times that μ occurs in the product $[1 \otimes 1]_{\lambda}$, $\lambda = \pm$, and $n_{\mu} = n^{+}_{\mu} + n^{-}_{\mu}$ then the number of terms occurring for a given η,ε can be shown to be

$$N^{\eta\varepsilon} = \frac{1}{2} \sum_{\mu} [(1-\varepsilon) n^{+}_{\mu} n^{-}_{\mu} + \frac{1}{2}(1+\varepsilon)(n^{+2}_{\mu} + n^{-2}_{\mu} + \eta n_{\mu} \delta_{\mu\mu^*})] \tag{2.44}$$

This reduces to

$$N^{++} = \frac{1}{2} \sum_{\mu} [n_{\mu}^{+2} + n_{\mu}^{-2} + n_{\mu} \delta_{\mu\mu*}]$$

$$N^{+-} = N^{--} = \sum_{\mu} n_{\mu}^{+} n_{\mu}^{-}$$

$$N^{-+} = \frac{1}{2} \sum_{\mu} n_{\mu}^{+2} + n_{\mu}^{-2} - n_{\mu} \delta_{\mu\mu*} \qquad (2.45)$$

These numbers agree with those found from the spherical basis as we would expect. However in the spherical basis we found that $N^{+-} = N^{-+} = N^{--}$ (figure 2.1). This is not obvious in this point group basis and suggests the relationship

$$\sum_{\mu} [(n_{\mu}^{+} - n_{\mu}^{-})^2 - n_{\mu} \delta_{\mu\mu*}] = 0 \qquad (2.46)$$

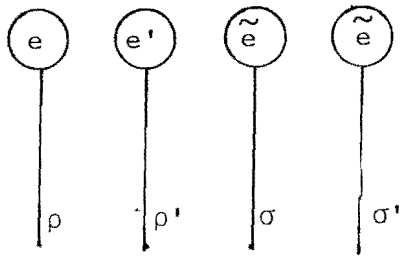
The existence of such a relationship is not obvious from the consideration of group properties.

The three bases may be summarised diagrammatically as in figure 2.2.

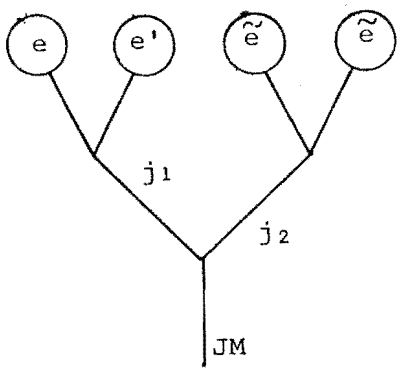
2.4 INDEPENDENT EXPERIMENTAL ARRANGEMENTS

We have shown that the intensity for a two photon experiment can be written in the form

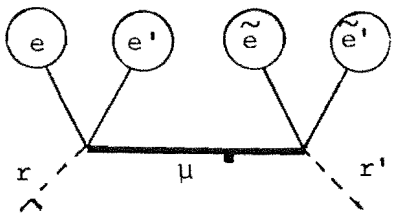
$$I(\underline{e}\ \underline{e}') = \sum_{\alpha} F_{\alpha}(\underline{e}\ \underline{e}')\ c_{\alpha}(\Omega) \qquad (2.47)$$



cartesian basis



spherical basis



point group basis

Figure 2.2: Summary of the three bases. The symmetrisations $\eta\varepsilon$ are omitted.

where the $c_\alpha(\Omega)$ can be chosen in different bases as independent real constants. We have derived the number of terms in the sum for different physical situations and for different point group symmetries (table 3). In this section we give a method for determining the $c_\alpha(\Omega)$ from experimental results. This requires equation 2.47 to be invertible i.e.

$$c_\alpha(\Omega) = \sum_{\underline{e}\,\underline{e}'} F_\alpha^{-1}(\underline{e}\ \underline{e}')\ I(\underline{e}\ \underline{e}') \qquad (2.48)$$

For this we need a set of polarisation vectors $(\underline{e}\ \underline{e}')$ for which the scattering intensities are independent.

Guided by the Stokes description of light (Shurcliff 1962), which describes the polarisation of a beam in terms of components which are (i) along cartesian axes (ii) at 45° to the axes and (iii) circularly polarised, we consider the nine polarisations given in figure 2.3.

$$\begin{array}{lll} x = (1,0,0) & D = \frac{1}{\sqrt{2}}(0,1,1) & G = \frac{1}{\sqrt{2}}(0,1,i) \\ y = (0,1,0) & E = \frac{1}{\sqrt{2}}(1,0,1) & H = \frac{1}{\sqrt{2}}(1,0,i) \\ z = (0,0,1) & F = \frac{1}{\sqrt{2}}(1,1,0) & I = \frac{1}{\sqrt{2}}(1,i,0) \end{array}$$

Figure 2.3: Polarisations needed for independent intensity measurements.

The 81 intensities $I(\underline{e}\ \underline{e}')$ where $\underline{e},\underline{e}'$ each take the nine values in figure 2.3 form a complete set. By this we mean that any other intensity measurement can be expressed as a linear combination of these 81 independent $I(\underline{e}\ \underline{e}')$ and so is superfluous. As an example consider $\underline{e} = X = (1,0,0)$, $\underline{e}' = L = (1,-i,0)$. By expanding in the cartesian basis (in this case unsymmetrised see equations 2.14, 2.15) we can show that

$$I(X,L) = c_{xxxx} + c_{xyxy} + i(c_{xxxy} - c_{xyxx})$$

One can easily check that this is equivalent to

$$I(X,L) = 2[I(X,X) + I(X,Y)] - I(X,I).$$

One can prove that the set is complete by expanding the intensity for general polarisation vectors $\underline{e} = (\alpha,\beta,\gamma)$, $\underline{e}' = (\alpha',\beta',\gamma')$ in a similar way.

This set of independent experimental arrangements could be chosen in an infinite number of ways, however this one is simply described and is convenient to use. The 81 independent $I(\underline{e}\ \underline{e}')$ are shown in figure 2.4.

The spherical basis is useful in helping to determine which of these spectra are independent in a particular situation. In the alternative coupling we couple $\underline{e}$ with $\tilde{\underline{e}}$ to angular momentum j_1. If $j_1 = 1$ then we are interested in the antisymmetric part of the coupling where $[\underline{e},\tilde{\underline{e}}]^{j_1=1} = -[\tilde{\underline{e}},\underline{e}]^{j_1=1}$. This term is non zero only if $\underline{e} \neq \tilde{\underline{e}}$ i.e. $\underline{e}$ is

circularly polarised. The three circularly polarised choices of $\underline{e},\underline{e}'$ correspond to the three components of j_1, $j_2 = 1$. There is no such restriction for the other values of j_1, j_2 and we choose the linear polarisations to correspond to the six components of $j_1, j_2 = 0,2$.

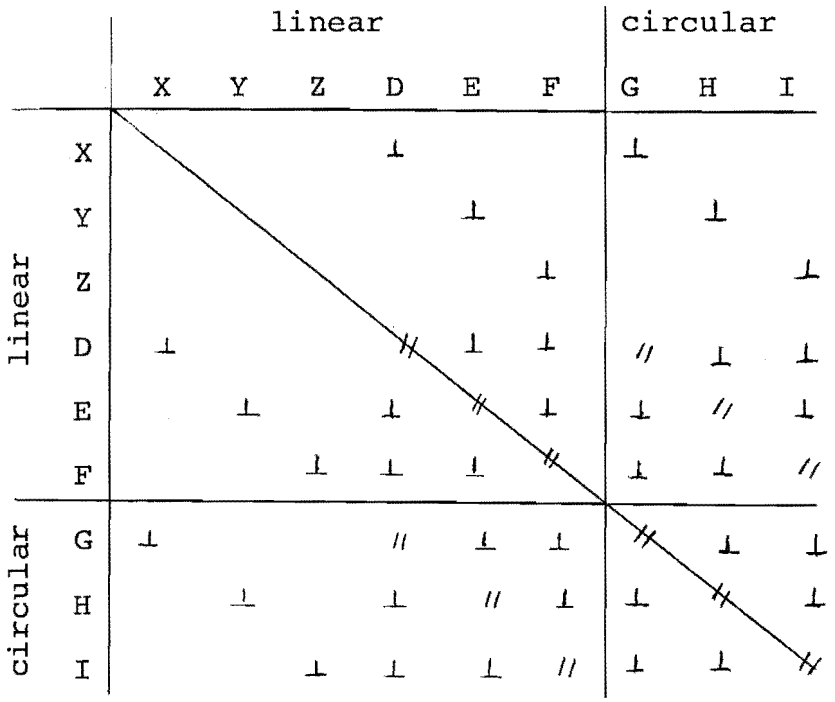


Figure 2.4: Independent intensities $I(\underline{e}\ \underline{e}')$. $\perp(\parallel)$ denotes that a 90° (180°) scattering geometry is required.

In the general case $j_1 j_2 JM$ can take all values and all 81 intensities will be independent. For real scatterers we have shown in section 2.3b (see figure 2.1) that in the alternative coupling j_1+j_2 is even, i.e. both polarisations

linear or both circular. The number of independent polarisations is therefore reduced to the 45 which appear in the two blocks along the diagonal of figure 2.4. The other intensities are no longer independent. For example, we can expand in the cartesian basis to show that

$$2I(\underline{X},\underline{G}) = I(\underline{X},\underline{X}) + I(\underline{X},\underline{Z}) \text{ for } \eta = +1$$

For the case of symmetric scatterers we have that $I(\underline{A},\underline{B}) = I(\underline{B},\underline{A})$ so that only those 45 intensities above and including the leading diagonal will be independent. Point group symmetry further reduces the number of independent polarisations required for any situation. For real symmetric scatterers the independent arrangements can be found for each point group in tables 9 or 10.

2.5 PHYSICAL CONSEQUENCES

With the set of independent experimental arrangements given in the last section we are now in a position to invert equation 2.47 to get

$$c_\alpha(\Omega) = \sum_\alpha (F_\alpha(\underline{e}\ \underline{e}'))^{-1} I(\underline{e}\ \underline{e}') \qquad (2.49)$$

The experimental results $I(\underline{e}\ \underline{e}')$ can be combined according to equation 2.49 to determine the physical constants $c_\alpha(\Omega)$. Once these constants have been determined the maximum information possible from polarisation studies will have been

obtained. We tabulate the matrices $(F_{\alpha}^{++}(ee'))^{-1}$ with $\alpha = \mu rr'$ for all point groups in table 10 and for $\alpha = j_1 j_2 JM$ in table 7. The matrices can also be determined in a cartesian basis from the information contained in tables 4-10 (see next section).

For real, symmetric scatterers the number of independent spectra is 27 for the general case. This number is reduced to the N^{++} associated with a particular point group symmetry leaving $27-N^{++}$ linear relationships connecting the remaining spectra. We list these relationships in table 11 enabling an experimenter to choose the N^{++} arrangements which are most convenient. These relationships may also prove to be useful in determining the point group symmetry of the scatterer. The results given here would enable the symmetry of a scatterer to be determined as belonging to one of the sets of groups given in table 11. The results could be extended to values of $\eta, \varepsilon \neq +1$ and to magnetic dipole coupling which would allow one to distinguish further groups within the sets by this method.

One of the more important consequences of the previous sections is the necessity of including measurements with circularly polarised light. Even for real symmetric scatterers circular polarisation choices are required for all point group symmetries. This is a consequence of the existence of the invariant term $J = 0$ in the product $(j_1 = 1) \otimes (j_2 = 1)$. Fröhlich et al (1970) pointed out the necessity for the use of circular polarisation for two

photon absorption in O_h symmetry. Our table 10 is essentially an extension of his analysis to all other point groups. Another point to note is the need for different scattering geometries. It is not possible, for instance, to achieve all the independent sets of polarisations by using the usual Raman scattering angle of 90°. It is necessary, for all symmetries to include some measurements with a 180° scattering angle. It is possible however for groups other than C_2, C_s, C_{2h}, to obtain all the independent arrangements for the real symmetric case by using only 180° measurements.

Another consequence of the restrictions imposed by various physical situations and symmetries is to do with symmetric scatterers. For $\varepsilon = +1$ we have in the standard coupling that j_1+j_2 must be even or equivalently in a point group basis $\{11\mu r\}\{11\mu r'\} = +1$. This means that although terms in the amplitude may be antisymmetric ($j_1 = 1$ or $\mu r \in [1 \times 1]-$) we have the restriction that the two amplitude contributions must be either both symmetric or both antisymmetric. This non interference of symmetric and antisymmetric terms means that antisymmetric amplitude terms can contribute without affecting the symmetry of the intensity. This is particularly important in a case such as the phonon Raman effect where degenerate electronic states can give rise to antisymmetric terms in the amplitude. Our analysis explains why authors such as Kiel et al (1969) failed to find corresponding antisymmetric

terms in the intensity for such a case. We discuss the phonon Raman effect in greater detail in the next chapter.

One final point concerns the symmetry groups R_3, K, O, O_h, and T_d. For these groups it is impossible to find invariant sets of labels α unless $\eta = \varepsilon = +1$ (see table 3). That is, the only contributions to the intensity will be real and symmetric. As there are no $\eta,\varepsilon = -1$ terms we would not expect any handed effects or any antisymmetric scattering in systems with this high degree of symmetry.

2.6 USE OF TABLES

The tables 4-10 can be summarised as in figure 2.5. The tables are only applicable for real symmetric scatterers $\eta = \varepsilon = +1$, and for electric dipole coupling.

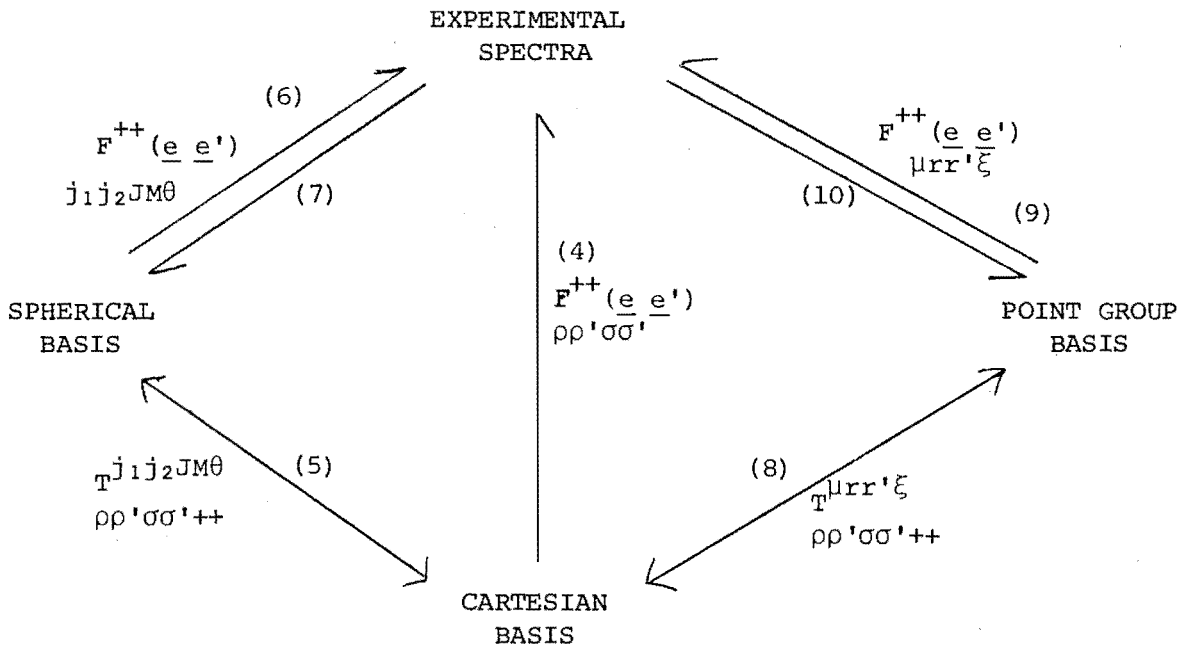


Figure 2.5: Information contained in Tables 4-10. Double ended arrows indicate an orthogonal transformation.

The orientation of the cartesian axes is defined by the transformation

$$|1^- \pm 1\rangle \equiv \frac{1}{\sqrt{2}} (y \mp ix)$$

$$|1^- 0\rangle \equiv iz \qquad (2.50)$$

and the transformation coefficients $\langle JM|J\lambda\mu\nu\rangle$ given by Butler (1981). In general the z axis will be the highest symmetry axis in the group-subgroup chain. For example in octahedral symmetry we choose the basis described by the chain $O\text{-}D_4\text{-}C_4$ and so the z axis will be the four-fold axis. Had we chosen the basis $O\text{-}D_3\text{-}C_3$ then the z axis would be the three-fold axis. The problem of the orientation of axes is discussed by Reid and Butler (1980).

As an example of the use of the tables we consider the octahedral group. From table 10 we immediately find the physical constants (in a point group basis) in terms of the irreducible spectra $I(\underline{e}\ \underline{e}')$. We have

$$c_{000} = XX - 2HH + 2DD$$

$$c_{200} = \sqrt{2}(XX + HH - DD)$$

$$c_{\tilde{1}00} = \sqrt{3}(-XX + HH + DD)$$

$$c_{100} = \sqrt{3}(XX + 2XY - HH - DD) \qquad (2.51)$$

We can get a similar set of equations for the spherical basis. Table 3 gives the four spherical labels that will

contribute for octahedral symmetry and we can use table 7 together with the relationships of table 11 to give

$$c_{0000} = XX + 2DD - 2HH$$

$$c_{1100} = \sqrt{3}\ (XX + 2XY - DD - HH)$$

$$c_{2200} = \frac{1}{\sqrt{5}}\ (-XX + DD + 5HH)$$

$$c_{224c} = \frac{12}{\sqrt{30}}\ (XX - DD) \qquad (2.52)$$

The connection between the constants in the point group basis and the cartesian basis can be found directly from table 8 and by multiplying the matrices in tables 8 and 10 we find that we have

$$c_{xxxx+} = \sqrt{3}\ XX$$

$$c_{xxyy+} = \sqrt{6}\ (DD - HH)$$

$$c_{xyxy+} = \sqrt{6}\ XY$$

$$c_{xyyx+} = \sqrt{6}\ (-XX - XY + DD + HH) \qquad (2.53)$$

where $xxxx+ = \frac{1}{\sqrt{3}}\ (xxxx + yyyy + zzzz)$ etc.

As well as these symmetrised cartesian labels we also give in table 8 the relationships between the unsymmetrised cartesian quartics under each point group symmetry. e.g. in this case we have that xxxx = yyyy = zzzz.

In this way one may determine the four physical constants c_α (with α in any of the three bases) from the

four independent experimental measurements I(XX), I(XY), I(H H), I(D D). Equation 2.51 amounts to the inverse of a submatrix of table 1 of Frölich et al. The extension of this analysis to all point groups fills a gap in the literature noted by Worlock (1972).

CHAPTER THREE

NON RESONANT VIBRATIONAL RAMAN EFFECT

We are now in a position to apply some of the results of the last chapter to a specific case. The theory for the phonon or vibrational Raman effect has been well known for the case of non degenerate electronic ground states since the work of Placzek in 1934. Selection rules for scattering off oriented and orientationally averaged centres have been tabulated by many authors (Loudon 1964, Ovander 1969, McClain 1971). We extend the methods of Loudon (1963) to include scattering off degenerate electronic ground states. The use of the rigorous group theoretical analysis described in the last chapter permits us to derive a selection rule that is consistent with that of Child (1962) but which is somewhat stronger. It allows us to prove that symmetric and anti-symmetric terms in the amplitude will not interfere in the non resonant case. We extend the well known selection rules for singlet electronic states, to cover all possible electronic states and phonon modes for all point groups. Diagram techniques are used to analyse the case of orientationally averaged scatterers.

3.1 SCATTERING AMPLITUDE

It is generally accepted (Loudon 1964) that the dominant contribution to the coupling between photons and phonons is mediated by the electrons in the scatterer. We therefore

consider two interactions: the electron-radiation interaction (H_{ER}) and the electron-lattice interaction (H_{EL}). Other interactions, for example radiation-lattice do not contribute significantly. Following Loudon (1963) we consider the scattering process in three steps.

1. destruction of an incident photon (H_{ER})
2. creation of a scattered photon (H_{ER})
3. creation of a phonon (H_{EL})

We can separate the operators responsible for these interactions into a part acting between electronic levels, and a part responsible for the creation or annihilation of the photons or phonons. For the electric dipole approximation the electronic parts of these interactions can be expressed in the form

$$H_{ER}^{\alpha\beta} \alpha \langle\beta|\underline{e}\cdot\underline{p}|\alpha\rangle$$

$$H_{EL}^{\alpha\beta} \alpha \langle\beta|V^{\kappa}|\alpha\rangle \qquad (3.1)$$

α,β label the electronic states, $\underline{e}$ is a polarisation vector, $\underline{p}$ is the momentum operator for the electron and V^{κ} is the electronic part of the interaction which creates a phonon of symmetry κ .

The first order scattering amplitude for an incident/scattered photon with polarisation vector $\underline{e}/\underline{e}'^{*}$ is given by

$$A = \sum_{\rho\rho'} e_{\rho} R_{\rho\rho'}^{k\ell\ell'}(\Omega) e'_{\rho'}, \qquad (3.2)$$

$R^{k\ell\ell'}_{\rho\rho'}(\Omega)$ is a generalisation of the Raman tensor and can be expressed by means of third order perturbation theory as

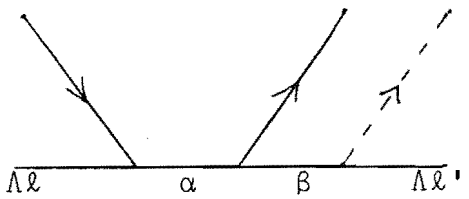
$$R^{k\ell\ell'}_{\rho\rho'}(\Omega) = \sum_{\alpha\beta} \frac{\langle\overline{\Lambda\ell}'|V^{\kappa}_{k}|\alpha\rangle\langle\alpha|p_{\rho'}|\beta\rangle\langle\beta|p_{\rho}|\Lambda\ell\rangle}{(\omega_{\beta}-\omega_{\Lambda}-\omega_{\kappa})(\omega_{\alpha}-\omega_{\Lambda}-\omega_{in})} + 5 \text{ terms} \qquad (3.3)$$

$\Omega = (-\omega_{in}, \omega_{out}, \omega_{\kappa})$ where ω_{in}/ω_{out} is the frequency of the incident/scattered photon and ω_{κ} is the phonon frequency. k enumerates the partners of the lattice mode κ , and ℓ,ℓ' label the partners of the electronic ground state Λ.

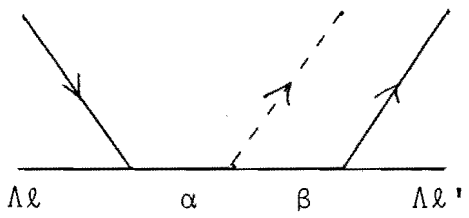
At this point we have generalised Loudon's formalism to include the situation where the electronic ground state is degenerate i.e. $\ell \neq \ell'$. Λ may be a reducible representation of the point group under consideration. It includes all energetically degenerate levels and so for an irreducible representation λ where $\lambda \neq \lambda^*$ (i.e. Kramers degeneracy) we let $\Lambda = \lambda + \lambda^*$. The bar over $\langle\overline{\Lambda\ell}'|$ indicates the time reversed state (see appendix A1) the five other terms correspond to the five alternative orderings of the three interactions. We list these diagrammatically in figure 3.1 where we use the shorthand $p^{\rho}_{\ell\alpha} = \langle\overline{\Lambda\ell}|p_{\rho}|\alpha\rangle$. From inspection of the six terms in Figure 3.1 we see that

$$R^{k\ell\ell'}_{\rho\rho'}(-\omega_{in},\omega_{out}, \omega_{\kappa}) = R^{k\ell\ell'}_{\rho'\rho}(\omega_{out}, -\omega_{in}, \omega_{\kappa}) \qquad (3.4)$$

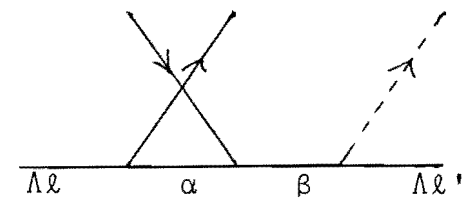
By considering the time reversal and hermiticity properties of the matrix elements (see appendix A1) we find that we also have the symmetry



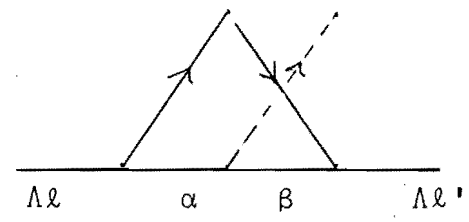
$$\frac{V^{\kappa}_{\ell',\beta} p^{\rho'}_{\beta\alpha} p^{\rho}_{\alpha\ell}}{(\omega_\alpha - \omega_\Lambda - \omega_{in})\,(\omega_\beta - \omega_\Lambda - \omega_\kappa)}$$



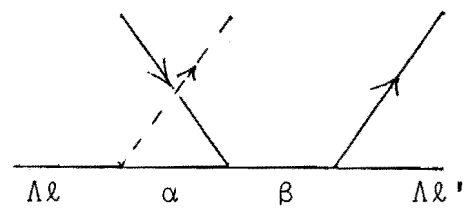
$$\frac{p^{\rho'}_{\ell',\beta} V^{\kappa}_{\beta\alpha} p^{\rho}_{\alpha\ell}}{(\omega_\alpha - \omega_\Lambda - \omega_{in})\,(\omega_\beta - \omega_\Lambda - \omega_{out})}$$



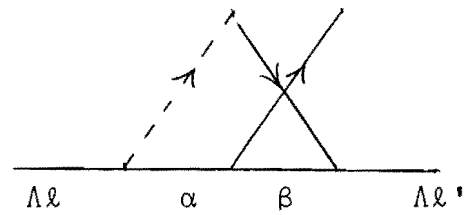
$$\frac{V^{\kappa}_{\ell',\beta} p^{\rho}_{\beta\alpha} p^{\rho'}_{\alpha\ell}}{(\omega_\alpha - \omega_\Lambda + \omega_{out})\,(\omega_\beta - \omega_\Lambda - \omega_\kappa)}$$



$$\frac{p^{\rho}_{\ell',\beta} V^{\kappa}_{\beta\alpha} p^{\rho'}_{\alpha\ell}}{(\omega_\alpha - \omega_\Lambda + \omega_{out})\,(\omega_\beta - \omega_\Lambda + \omega_{in})}$$



$$\frac{p^{\rho'}_{\ell',\beta} p^{\rho}_{\beta\alpha} V^{\kappa}_{\alpha\ell}}{(\omega_\alpha - \omega_\Lambda + \omega_\kappa)\,(\omega_\beta - \omega_\Lambda - \omega_{out})}$$



$$\frac{p^{\rho}_{\ell',\beta} p^{\rho'}_{\beta\alpha} V^{\kappa}_{\alpha\ell}}{(\omega_\alpha - \omega_\Lambda + \omega_\kappa)\,(\omega_\beta - \omega_\Lambda + \omega_{in})}$$

Figure 3.1: Terms in first order Raman scattering amplitude.

$$R^{k\ell\ell'}_{\rho\rho'}(\omega_{in},\omega_{out},\omega_K) = \tau_\Lambda\, R^{k\ell'\ell}_{\rho\rho'}(\omega_{in},-\omega_{out},-\omega_K) \qquad (3.5)$$

Combining equations 3.4 and 3.5 we find.

$$R^{k\ell\ell'}_{\rho\rho'}(\Omega) = \tau_\Lambda\, R^{k\ell'\ell}_{\rho'\rho}(\Omega') \qquad (3.6)$$

where $\Omega = (-\omega_{in},\ \omega_{out},\ \omega_K)$, $\Omega' = (-\omega_{out},\ \omega_{in},\ -\omega_K)$.

From energy considerations we have that $\omega_{in} = \omega_K + \omega_{out}$. Since phonon energies are much smaller than photon energies i.e. $\omega_K << \omega_{in},\ \omega_{out}$ it is reasonable to replace ω_K by zero in the denominators if we are far from resonance i.e. $\omega_\alpha - \omega_\Lambda - \omega_{in} \neq 0$. In this situation we have $\omega_{in} \approx \omega_{out}$ and

$$R^{k\ell\ell'}_{\rho\rho'}(\Omega) \approx \tau_\Lambda\, R^{k\ell'\ell}_{\rho'\rho}(\Omega) \qquad (3.7)$$

In general therefore the amplitude is not symmetric. For the case of a non degenerate electronic ground state we have $\ell = \ell'$, $\tau_\Lambda = +1$ so that

$$R^{k}_{\rho\rho'}(\Omega) = R^{k}_{\rho'\rho}(\Omega) \qquad (3.8)$$

and the amplitude is symmetric with respect to the polarisations of the incident and scattered photons. This is the result obtained by Loudon.

From our time reversal and hermiticity considerations we have generalised the results of Loudon and shown that a degenerate electronic ground state can cause non symmetric terms in the Raman scattering amplitude.

3.2 SCATTERING INTENSITY

We now consider the symmetry properties of the scattering intensity. The intensity is given by the square of the amplitude i.e.

$$I(\underline{e}\ \underline{e}') = \sum_{k\ell\ell'} \Big| \sum_{\rho\rho'} e_\rho\ R^{k\ell\ell'}_{\rho\rho'}(\Omega) e'_{\rho'} \Big|^2 \qquad (3.9)$$

The sum over $k\ell\ell'$ takes into account the possibility of scattering from or to different partners of the possibly degenerate states Λ and κ. If we interchange the incident and scattered polarisations we have

$$I(\underline{e}'\ \underline{e}) = \sum_{k\ell\ell'} \Big| \sum_{\rho\rho'} e'_\rho\ R^{k\ell\ell'}_{\rho'\rho}\ e_\rho \Big|^2$$

$$= \sum_{k\ell\ell'} \Big| \sum_{\rho\rho'} e_\rho\ R^{k\ell'\ell}_{\rho\rho'}\ e'_{\rho'}\ \tau_\Lambda \Big|^2 \qquad (3.10)$$

where we have used equation 3.7. From this we can see that the intensity has the symmetry

$$I(\underline{e}'\underline{e}) = I(\underline{e}\ \underline{e}') \qquad (3.11)$$

This means that the non resonant phonon Raman effect is a

symmetric scattering process i.e. $\varepsilon = +1$ (see §2.2). Although asymmetric amplitude terms may contribute this does not affect the symmetric properties of the intensity (see §2.5).

We also consider the intensity for the conjugated polarisation vectors. We have

$$I(\underset{\sim}{\tilde{e}}\ \underset{\sim}{\tilde{e}}') = \sum_{k\ell\ell'} \sum_{\rho\rho'\sigma\sigma'} \tilde{e}_\rho\ \tilde{e}'_\rho,\ e_\sigma e'_\sigma,\ R^{k\ell\ell'}_{\rho\rho'} (R^{k\ell\ell'}_{\sigma\sigma'})^* \qquad (3.12)$$

We can show (appendix A2) that $\sum_{k\ell\ell'} R^{k\ell\ell'}_{\rho\rho'} (R^{k\ell\ell'}_{\sigma\sigma'})^*$ is a real quantity and so we have that

$$I(\underset{\sim}{e}\ \underset{\sim}{e}') = I(\underset{\sim}{\tilde{e}}\ \underset{\sim}{\tilde{e}}') \qquad (3.13)$$

For the case of non resonant phonon Raman scattering therefore, we have that $\eta = \varepsilon = +1$ i.e. it is a real symmetric scattering process. We can now use the formalism of chapter 2 and the tables to deduce the number of independent constants which will contribute for any point group. We can go further however and deduce selection rules for particular phonon and electronic symmetries. This will further restrict the number of independent constants.

3.3 DERIVATION OF SELECTION RULES

The selection rules for the Raman scattering amplitude are well known for the case of a non degenerate electronic ground state (Loudon 1964, Ovander 1969, McClain 1971). We

extend these rules to include the case of a degenerate electronic ground state.

To deduce the symmetry properties of the scattering amplitude we couple the three operators together. The photon operators p_ρ transform as $j = 1^-$ of O_3 and the phonon operator V^K transforms as the representation κ^* of the point group. Using the reducible 3JM factors defined in equation 2.34 we can couple the operators as

$$V^K_k p^1_\rho p^1_{\rho'} = \sum_{\substack{\mu m \nu n \\ rs}} [V^K [p^1 p^1]^\mu_m]^\nu_n \begin{pmatrix} 1 & 1 & \mu^* \\ \rho & \rho' & m^* \end{pmatrix} r \begin{pmatrix} \mu & \kappa^* & \nu^* \\ m & k^* & n^* \end{pmatrix} s \begin{pmatrix} \mu \\ m \end{pmatrix} \begin{pmatrix} \nu \\ n \end{pmatrix}$$

$$|\mu|^{-\frac{1}{2}} |\nu|^{-\frac{1}{2}} \tag{3.14}$$

We can now use the Wigner-Eckart theorem to write the scattering amplitude in the form

$$R^{k\ell\ell'}_{\rho\rho'}(\Omega) = \sum_{\substack{\mu\nu\underline{r} \\ mn}} \begin{pmatrix} 1 & 1 & \mu^* \\ \rho & \rho' & m^* \end{pmatrix} r \begin{pmatrix} \mu & \kappa^* & \nu^* \\ m & k^* & n^* \end{pmatrix} s \begin{pmatrix} \Lambda & \nu & \Lambda \\ \ell' & n & \ell \end{pmatrix} t \begin{pmatrix} \mu \\ m \end{pmatrix} \begin{pmatrix} \nu \\ n \end{pmatrix}$$

$$|\mu|^{-\frac{1}{2}} |\nu|^{-\frac{1}{2}} f_{\mu\nu\underline{r}}(\Lambda, \kappa, \Omega) \tag{3.15}$$

where $\underline{r}$ stands for all the multiplicities r,s,t. The sum over intermediate states and the denominators are invariant under the point group operations, and the energy dependence is included in the constants $f_{\mu\nu\underline{r}}(\Lambda,\kappa,\Omega)$. By using recoupling coefficients (6j symbols) to reorder the operators we can express all six terms in the amplitude in this form. These 6j symbols and also the reduced matrix elements from the Wigner-Eckart theorem are included in the

constants $f_{\mu\nu\underline{r}}(\Lambda,\kappa,\Omega)$. These constants have the form

$$f_{\mu\nu\underline{r}}(\Lambda,\kappa,\Omega) \propto \langle\Lambda\|O^{\nu}\|\Lambda\rangle_t \langle 1\|O^{\mu}\|1\rangle_r \langle\mu\ r\ \|O^{\kappa}\|\nu t\rangle_s \qquad (3.16)$$

For non degenerate ground states, $|\Lambda| = 1$ and we have that $\Lambda \otimes \Lambda = 0$ (0 is the identity representation for the group) and so from equation 3.15 we must have $\nu = 0$ and $\mu = \kappa$ if the amplitude is to be non zero. The expression for the scattering amplitude reduces to

$$R^{\kappa}_{\rho\rho'}(\Omega) = \sum_r \begin{pmatrix} 1 & 1 & \kappa^* \\ \rho & \rho & k^* \end{pmatrix}_r f_{\kappa\underline{o}r}(\Lambda,\kappa,\Omega) \qquad (3.17)$$

Using the symmetry of $R^{\kappa}_{\rho\rho'}$, (equation 3.8) we see that we have the selection rule $\kappa \in [1 \times 1]_+$. The $R^{\kappa}_{\rho\rho'}$ are the tensor elements tabulated by Loudon, McClain and others.

We can generalise these selection rules to the degenerate case. From equation 3.15 we see that we must have

$$\begin{aligned} \mu_r &\in 1 \otimes 1 \\ \mu_s &\in \kappa \otimes \nu \\ \nu_t &\in \Lambda \otimes \Lambda \end{aligned} \qquad (3.18)$$

We also have from equation 3.15 that

$$R^{k\ell\ell'}_{\rho\rho'}(\Omega) = \{11\mu r\}\{\Lambda\Lambda\nu t\}\ R^{k\ell'\ell}_{\rho'\rho}(\Omega) \qquad (3.19)$$

The symmetry of $R^{k\ell\ell'}_{\rho\rho'}(\Omega)$ which we previously derived (equation 3.7) together with the above gives the restriction that

$$\tau_\Lambda\{11\mu r\}\{\Lambda\Lambda\nu t\} = 1 \tag{3.20}$$

for the non resonant case. The selection rules are therefore further restricted to

$$\begin{aligned} \mu_r &\in [1 \otimes 1]_\eta \\ \mu_s &\in \kappa \otimes \nu \\ \nu_t &\in [\Lambda \times \Lambda]_{\eta\tau_\Lambda} \end{aligned} \tag{3.22}$$

where $\eta = \pm 1$. These selection rules are consistent with those of Child (1962) although the inclusion of the multiplicity labels makes them somewhat stronger and allows us to prove further results.

Barron and Nørby Svendson (1980) use time reversal arguments to deduce a selection rule which is also equivalent to that of Child.

The expression for the amplitude depends on the partners $\ell\ell'$ of the degenerate electronic state. For this reason we find it more economical to derive selection rules for the intensity where this dependence has been summed out. Using equations 3.15 and 3.9 we can employ the orthogonality of the 3JM factors to write the intensity as

$$I(\underline{e}\ \underline{e}') = \sum_{\mu rr'} F_{\mu rr'}(\underline{e}\ \underline{e}')\ c_{\mu rr'}(\Lambda\kappa\Omega) \tag{3.23}$$

where

$$c_{\mu rr'}(\Lambda\kappa\Omega) = \sum_{\nu st} f_{\mu\nu\underline{r}}(\Lambda\kappa\Omega)\ f^{*}_{\mu\nu\underline{r}'}(\Lambda\kappa\Omega)\,|\mu|^{-\frac{1}{2}} \tag{3.24}$$

and

$$F_{\mu rr'}(\underline{e}\ \underline{e}') = \sum_{n} |\mu|^{\frac{1}{2}} \begin{pmatrix} 1 & 1 & \mu \\ \rho & \rho' & n \end{pmatrix} r \begin{pmatrix} 1 & 1 & \mu \\ \sigma & \sigma' & n \end{pmatrix}^{*} r'\ e_{\rho}e'_{\rho},\ \tilde{e}_{\sigma}\tilde{e}_{\sigma'} \tag{3.25}$$

and $\underline{r} = (r,s,t)$, $\underline{r}' = (r',s,t)$.

This is of course exactly the form of the intensity we derived in §2.3c for a real symmetric scatterer. From our results in chapter two and also from equations 3.23 and 3.11 we have

$$\{11\mu r\}\{11\mu r'\} = +1 \tag{3.26}$$

This is the restriction which makes our selection rules with their explicit dependence on the multiplicity labels stronger than those of Child. It is also the reason why the intensity remains symmetric even though antisymmetric amplitude terms may contribute (§2.5).

Given a particular electronic ground state Λ and phonon symmetry κ the selection rules (equations 3.22 and 3.26) restrict the values of $\mu rr'$ which will contribute to the intensity (equation 3.23). In table 12 we give the values of $\mu rr'$ which will contribute to the intensity for any choice of Λ and κ in any point group. All singlet states $|\Lambda| = 1$ have the same selection rules and these are tabulated together as $\Lambda = 0$.

In special cases the number of constants can be reduced even further. We have that

$$c_{\mu rr'} = \sum_{\nu st} f_{\mu\nu\underline{r}} f^{*}_{\mu\nu\underline{r}'} |\mu|^{-\frac{1}{2}} , \tag{3.27}$$

When there is only one term in the sum over νst the constant is factorisable i.e.

$$c_{\mu rr'} = a_r a^{*}_{r'} \tag{3.28}$$

and we have the relationship

$$c_{\mu rr'} c_{\mu r'r} = c_{\mu rr} c_{\mu r'r'} \quad . \tag{3.29}$$

This reduces the number of independent constants even further. The cases for which equation 3.29 holds are denoted in table 12 with an asterisk. Relationships such as equation 3.29 illustrate the value of making a rigorous group theoretical analysis with the inclusion of all phases and multiplicities. Such a relationship is not at all obvious from a casual analysis.

Once one has determined which independent values of μrr' will contribute for a given situation then table 10 can be used to find the experimental arrangements necessary to determine the values of the independent physical constants. We include an example in the next section.

3.4 EXPERIMENTAL CONSEQUENCES

In this section we consider the effect a degenerate electronic ground state may have on experimental results and we interpret the results of Johnstone and Dubicki (1980).

We have the general expression for the intensity

$$I(\underline{e}\ \underline{e}') = \sum_{\mu rr'} F_{\mu rr'}\ (\underline{e}\ \underline{e}')\ c_{\mu rr'}(\Lambda,\kappa,\Omega) \qquad (3.30)$$

which in the non degenerate case reduces to

$$I(\underline{e}\ \underline{e}') = \sum_{rr'} F_{\kappa rr'}\ (\underline{e}\ \underline{e}')\ c_{\kappa rr'}(\Lambda\kappa\Omega) \qquad (3.31)$$

The selection rules (equations 3.22) show that μ will always be able to take the value $\mu = \kappa$ in equation 3.30. For a degenerate ground state therefore we will still have all the terms expected in the non degenerate case i.e. $\mu = \kappa$, but in general there will be additional terms corresponding to $\mu \neq \kappa$.

The constants $c_{\mu rr'}(\Lambda,\kappa,\Omega)$ are a function of the photon and phonon frequencies. The fact that most experimental results seem to be in accordance with the non degenerate selection rules of Loudon suggests that the frequency dependence is such that the extra terms may not contribute significantly to the spectra.

The results of Johnstone and Dubicki (1980) for phonon Raman scattering off $CsCoBr_3$ however may be an example of a contribution from the extra terms expected in the degenerate case. The cobalt ion has a degenerate ground state

$\Lambda = \frac{1}{2}(\Gamma_4)$ of D_{3d} symmetry and this is thought to be responsible for the scattering. Johnstone et al found a contribution to the $\kappa = 0(A_{1g})$ phonon for polarisations $\underline{e} = Y = (0,1,0)$, $\underline{e}' = X = (1,0,0)$ which they did not expect from the usual non degenerate selection rules of Loudon. This effect was not observed in $CsMgBr_3$ which has a singlet electronic ground state. From our selection rules (table 12) we have the following constants contributing for the two ground states.

$CsMgBr_3$ $\Lambda = 0$ $\kappa = 0$ $\mu rr' = 000, 001, 011$

$CsCoBr_3$ $\Lambda = \frac{1}{2}$ $\kappa = 0$ $\mu rr' = 000, 001, 011, 122, \tilde{0}00$

The submatrix of interest from table 9 for D_{3d} is, for the polarisations considered by Johnstone et al.

	000	001	011	122	$\tilde{0}00$
XX	✓	✓	✓		
XY					✓
XZ				✓	

For $\Lambda = 0$ as in $CsMgBr_3$ we only expect to see the $\kappa = 0$ phonon for XX polarisations whereas for $\Lambda = \frac{1}{2}$ as in $CsCoBr_3$ we do expect a contribution to the XY and XZ spectra. Our

selection rules therefore do account for the otherwise unexpected observation of the $\kappa = 0$ phonon for XY polarisations. More sensitive experiments may uncover many more occasions where a degenerate electronic state causes additional contributions to the spectra.

It is worthwhile noting that Johnstone and Dubicki observed no asymmetric scattering i.e. their results for XZ and ZX polarisations were identical as we would predict. We also note that their measurement for polarisations YZ was superfluous in this case. The relationships between intensity measurements (table 11) predict that XZ = YZ for D_{3d}, and the experimental results bear this out.

This analysis shows how the results of chapter two and the selection rules derived in this chapter may be used to interpret experimental data, and also to determine what experimental measurements are necessary. It is hoped that these selection rules will facilitate the identification of phonon modes and also enable the determination of the electronic ground states of the scatterer.

3.5 ORIENTATIONALLY AVERAGED SCATTERERS

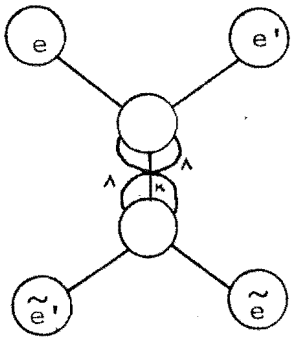
The results of the previous sections can also be applied to Raman scattering in fluids, vapours and powders. In these situations the scattering molecules are randomly oriented with respect to the incident and scattered light beams. We find it useful in this situation to use diagram

methods (Stedman (1975)). This eliminates the need for averaging of direction cosines (Sushchinskii 1972, Monson and McClain 1970). This type of approach has been used by other workers e.g. Yuratich and Hanna (1976).

(a) Selection rules

Our expression for the intensity derived earlier can be expressed both algebraically and diagrammatically. We have

$$I(\underline{e}\ \underline{e}') = \sum_{k\ell\ell'} \Big| \sum_{\rho\rho'} e_\rho\ R^{k\ell\ell'}_{\rho\rho'}\ e'_{\rho'} \Big|^2 \qquad (3.32)$$

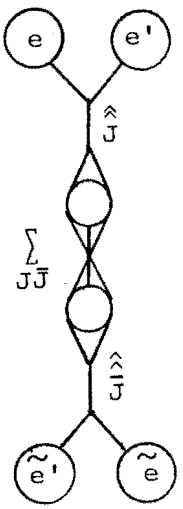


We can couple the operators to angular momentum J (as in §2.3b) by inserting the identity

$$\sum_{JM} \begin{pmatrix} 1 & 1 & J \\ \rho & \rho' & M \end{pmatrix} \begin{pmatrix} 1 & 1 & J \\ \sigma & \sigma' & M \end{pmatrix} \hat{\hat{J}} = \delta_{\rho\sigma}\ \delta_{\rho'\sigma'} \qquad (3.33)$$

where $\hat{\hat{J}} = (\hat{J})^2 = |J|$.

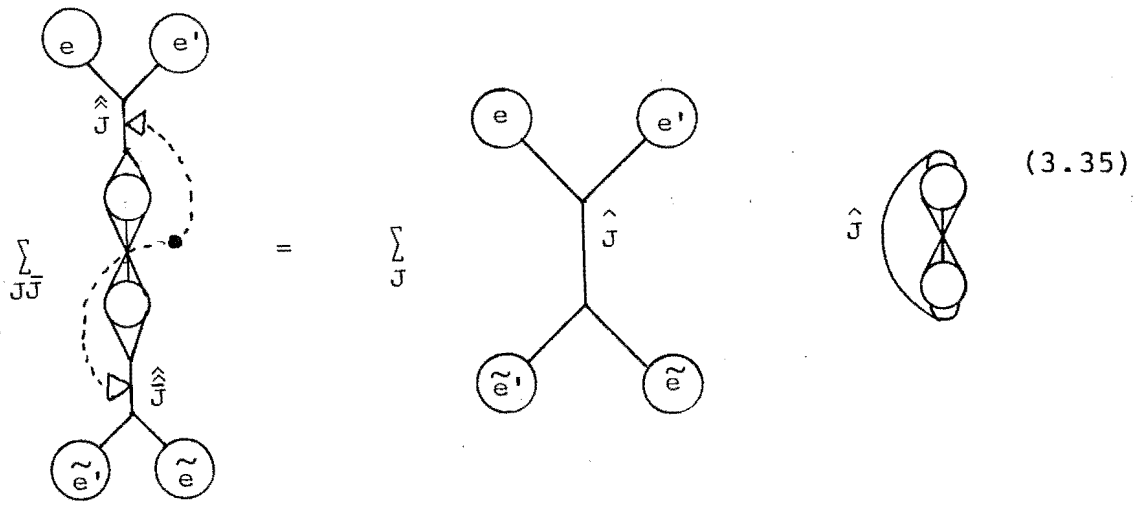
$$I(\underline{e}\ \underline{e}') = \sum_{k\ell\ell'} \Big| \sum_{\sigma\sigma' JM} [\underline{e}\ \underline{e}']^J_M\ R^{k\ell\ell'}_{\sigma\sigma'} \begin{pmatrix} 1 & 1 & J \\ \sigma & \sigma' & M \end{pmatrix} \hat{\hat{J}} \Big|^2 \qquad (3.34)$$



where

$$[\underline{e}\ \underline{e}']^J_M = \sum_{\rho\rho'} e_\rho e_{\rho'} \begin{pmatrix} 1 & 1 & J \\ \rho & \rho' & M \end{pmatrix}$$

Applying a group operation of SO_3 and averaging over the group elements gives us the situation required for randomly oriented scatterers. By doing this and using the great orthogonality theorem we find $J = \bar{J}$ or diagrammatically



(3.35)

Algebraically we write

$$I(\underline{e}\ \underline{e}') = \sum_J F_J(\underline{e}\ \underline{e}')C_J(\Omega) \tag{3.36}$$

where

$$F_J(\underline{e}\ \underline{e}') = \sum_M [\underline{e}\ \underline{e}']^J_M\ [\tilde{\underline{e}}\ \tilde{\underline{e}}']^J_M\ \hat{J} \tag{3.37}$$

$$C_J(\Omega) = \sum_{M'k\ell\ell'} \left| \sum_{\sigma\sigma'} R^{k\ell\ell'}_{\sigma\sigma'} \begin{pmatrix} 1 & 1 & J \\ \sigma & \sigma' & M' \end{pmatrix} \right|^2 \hat{J} \tag{3.38}$$

These equations are analogous to those for oriented scatterers equations 3.23 - 3.25 except that multiplicity labels are not required in the rotation group. The sum over J in equation 3.36 is over the values J = 0, 1, 2. This is essentially the result obtained by Placzek (1934). Our C_0, C_1, C_2 correspond (with normalisation) to his trace scattering G^o, antisymmetric G^a and quadrupole scattering G^s.

Monson and McClain (1970) also have an expression for the intensity as a product of geometrical and physical parts. We discuss the relationship between their constants and our C_J later.

The constants C_J will be non zero if the scattering amplitude $R^{k\ell\ell'}_{\sigma\sigma'}(\Omega)$ is non zero. We therefore have the selection rules (equations 3.22 and 3.26) as in the previous sections. We can expand the expression for C_J using the definition of $R^{k\ell\ell'}_{\rho\rho'}$ (equations 3.15) and find that it reduces to the form

$$C_J \propto \sum_{nm\mu\nu} \left| \sum_{\rho\rho' r} \begin{pmatrix} 1 & 1 & \mu \\ \rho & \rho' & n \end{pmatrix} r \; f_{\mu\nu r} \begin{pmatrix} 1 & 1 & J \\ \rho & \rho' & M \end{pmatrix} \right|^2 \qquad (3.39)$$

Using our definition of the reducible 3JM (equations 2.33, 2.34) and using the orthogonality of the 3JM factors we find that

$$C_J \propto \sum_{nm\mu\nu} \left| \sum_{n} f_{\mu\nu r} \langle JM|\mu nr\rangle |J|^{-1} \right|^2 \qquad (3.40)$$

For C_J to be non zero therefore the angular momentum J must branch to the representation μ in the point group. μ must also obey the selection rules (3.22 and 3.26) for a given Λ and κ. We tabulate the C_J which will contribute for particular electronic states and phonon modes in table 13 for all point groups. Child (1962) gives those values of Λ,κ (for Λ a spin representation) which give rise to a $J = 1$ contribution. Our selection rule agrees with Child's and we include corrections to his table 1 for the groups

(C_{4v}, D_{2d}, D_{4h}, D_{6h}). Our rules (and Child's) disagree with the results of Parameswaram et al (1977) for the octahedral group. The approach of these authors for the case of electronic degeneracy is to reduce to a lower symmetry group which lifts the degeneracy. However they ignore contributions which correspond to vibrational-electronic coupling in the lower symmetry group. There seems to be no justification for neglecting these contributions.

For the case of non degenerate electronic ground states we had the selection rule $\mu = \kappa \in [1 \otimes 1]_+$. μ must therefore branch from the symmetric part of $J = 1 \otimes 1$ i.e. $J = 0,2$. In this case there will be no contribution from the terms C_J with $J = 1$. As in the case for oriented scatterers the presence of a degenerate electronic ground state permits asymmetric amplitude terms i.e. allows C_1 terms.

(b) Geometrical Factors

We have the expression for the geometrical factors $F_J(\underline{e}\ \underline{e}')$

$$F_J(\underline{e}\ \underline{e}') = \sum_m \left| \sum_{\rho\rho'} e_\rho e'_{\rho'} \begin{pmatrix} 1 & 1 & J \\ \rho & \rho' & M \end{pmatrix} \right|^2 \hat{J} \qquad (3.41)$$

It is useful to consider the form of these factors for the different values of J. For the contrastandard transformation (equation 2.22) we have that for α,β,γ in a cartesian basis

$$\begin{pmatrix} 1 & 1 & 0 \\ \alpha & \beta & 0 \end{pmatrix} = \frac{1}{\sqrt{3}} \delta_{\alpha\beta}$$

$$\begin{pmatrix} 1 & 1 & 1 \\ \alpha & \beta & \gamma \end{pmatrix} = \frac{1}{\sqrt{6}} \varepsilon_{\alpha\beta\gamma} \qquad (3.42)$$

i.e. the J = 0 term corresponds to a scalar product while the J = 1 term corresponds to a vector product of the polarisations vectors. We have

$$F_0(\underline{e}\ \underline{e}') = \frac{1}{3} |\underline{e}\cdot\underline{e}'|^2$$

$$F_1(\underline{e}\ \underline{e}') = \frac{1}{2\sqrt{3}} |\underline{e} \times \underline{e}'|^2$$

$$= \frac{1}{2\sqrt{3}} (1 - |e\cdot e'^*|^2) \qquad (3.43)$$

We can determine the J = 2 term by considering the orthogonality properties of the 3JM factors. We find that

$$F_2(\underline{e}\ \underline{e}') = \frac{1}{\sqrt{5}} (\frac{1}{2} - \frac{1}{3}|e\cdot e'|^2 + \frac{1}{2}|e\cdot e'^*|^2) \qquad (3.44)$$

We see that the geometrical factors depend only on the two variables $\underline{e}\cdot\underline{e}'$ and $\underline{e}\cdot\underline{e}'^*$. This is the same result obtained by Monson and McClain (1970), McClain (1971) but without the need for averaging direction cosines.

The relative sizes of the constants C_J may therefore be determined by measurements involving different proportions of $\underline{e}\cdot\underline{e}'$ and $\underline{e}\cdot\underline{e}'^*$. The need for circular polarisations is

obvious as at least one measurement is required for which $\underline{e}' \neq \underline{e}'^*$. Placzek recognised the need for circularly polarised light and suggested two measurements, the depolarisation ratio and the reversal ratio, which would give the ratios of the three constants. In table 10 for R_3 derived in the last chapter we suggest the three independent measurements I(X X), I(X Y) and I(R R) where $R = \frac{1}{\sqrt{2}}(1,i,0)$ stands for right hand circularly polarised light. We have from table 10 a means of determining the constants i.e.

$$c_o = 3I(X\ X) - 2I(R\ R)$$

$$c_1 = 2\sqrt{3}\ I(X\ Y) - \sqrt{3}\ I(R\ R)$$

$$c_2 = \sqrt{5}\ I(R\ R) \qquad (3.45)$$

These results can also be obtained from the expression for $I(\underline{e}\ \underline{e}')$ (equation 3.36) and the values of $F(\underline{e}\ \underline{e}')$ (equations 3.43 and 3.44) which give the intensity in the the form

$$I(\underline{e}\ \underline{e}') = \frac{1}{3}|\underline{e}\cdot\underline{e}'|^2 c_o + \frac{1}{2\sqrt{3}}(1 - |\underline{e}\cdot\underline{e}'^*|^2)c_1$$

$$+ \frac{1}{\sqrt{5}}(\frac{1}{2} - \frac{1}{3}|\underline{e}\cdot\underline{e}'|^2 + \frac{1}{2}|\underline{e}\cdot\underline{e}'^*|^2)c_2 \qquad (3.46)$$

The traditional measurements are defined as follows. The depolarisation ratio ρ is

$$\rho = \frac{I(X,Y)}{I(X,X)} \tag{3.47}$$

and the reversal ratio $\mathbb{P}$ (for forward scattering i.e. $\theta=0°$)

$$\mathbb{P} = \frac{I(R,R)}{I(R,L)}$$

where $L = \frac{1}{\sqrt{2}}$ (1, -i, 0) is left hand polarised light. From our expression for $I(\underline{e}\,\underline{e}')$ equation 3.46 it is simple to show that

$$\rho = \frac{5\sqrt{3}\ c_1 + 3\sqrt{5}\ c_2}{4\sqrt{5}\ c_2 + 10\ c_o}$$

$$\mathbb{P} = \frac{6\sqrt{5}\ c_2}{5\sqrt{3}\ c_1 + 5\sqrt{c_2} + 10\ c_o} \tag{3.48}$$

which are equivalent to the expressions obtained in standard works e.g. Sushchinskii (1972). These expressions enable us to find the relationships between our c_J and the G^o, G^a, G^s of Placzek and the δf, δg, δh, of McClain. The relationships are

$$\begin{aligned} c_o = G_o &= \frac{1}{3}\,\delta f \\ \sqrt{3}\ c_1 = G_a &= \frac{1}{2}\,(\delta g - \delta h) \\ \sqrt{5}\ c_2 = G_s &= \frac{1}{2}\,(\delta g + \delta h) - \frac{1}{3}\,\delta f \end{aligned} \tag{3.49}$$

To summarise:- we have used a group theoretical analysis to extend the treatment of orientationally

averaged Raman scattering to the case where we have a degenerate electronic ground state. We derive a selection rule which is in agreement with that of Child (1962). By casting the geometrical factors in terms of scalar products of polarisation vectors we have a simple method for recovering standard results.

CHAPTER 4

NON LINEAR PROCESSES

Recent advances in laser technology have greatly increased the interest in non linear processes. In this chapter we show how the techniques of the previous sections can be extended to these higher order effects. We consider in detail the hyper Raman effect. We derive an expression for the intensity in terms of scalar products of polarisation vectors and obtain a generalisation of the result of Andrews and Thirunamachandran (1978). We also generalise the selection rules to cover the case of degenerate electronic levels. We give a brief account of how our symmetry considerations may be applied to coherent anti-Stokes Raman scattering (C.A.R.S.).

4.1 HYPER RAMAN EFFECT

(a) Reduction of scattering intensity

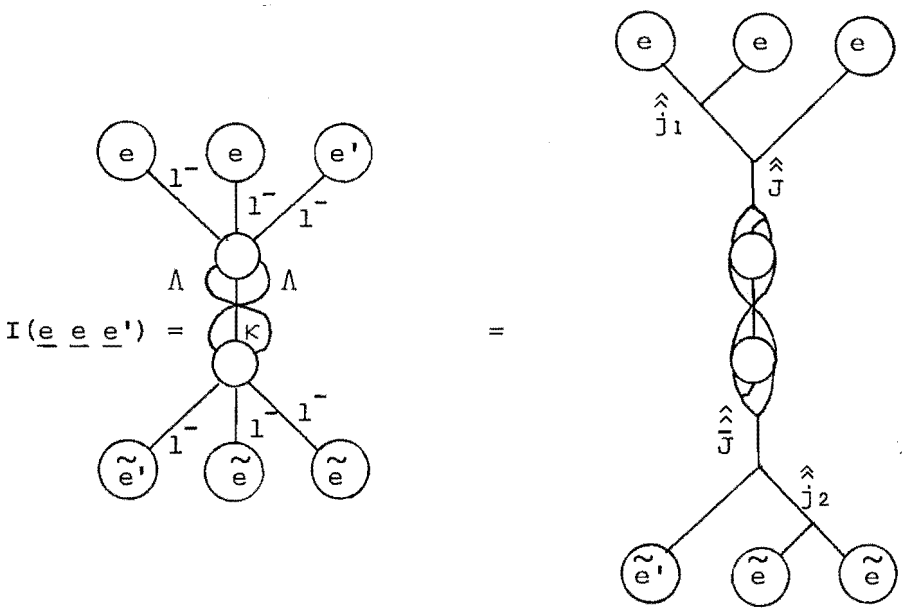
The hyper Raman effect involves two incident photons $\underline{e}_1, \underline{e}_2$ and one scattered photon $\underline{e}'^*$. We consider the most common situation where the incident photons are identical $\underline{e}_1 = \underline{e}_2 = \underline{e}$. The intensity can be written as

$$I(\underline{e}\ \underline{e}\ \underline{e}') = \sum_{k\ell\ell'} \Big| \sum_{\rho\sigma\tau} e_\rho\, e_\sigma\, e'_\tau\, R^{k\ell\ell'}_{\rho\sigma\tau}(\Omega) \Big|^2 \qquad (4.1)$$

For identical incident photons the third rank tensor

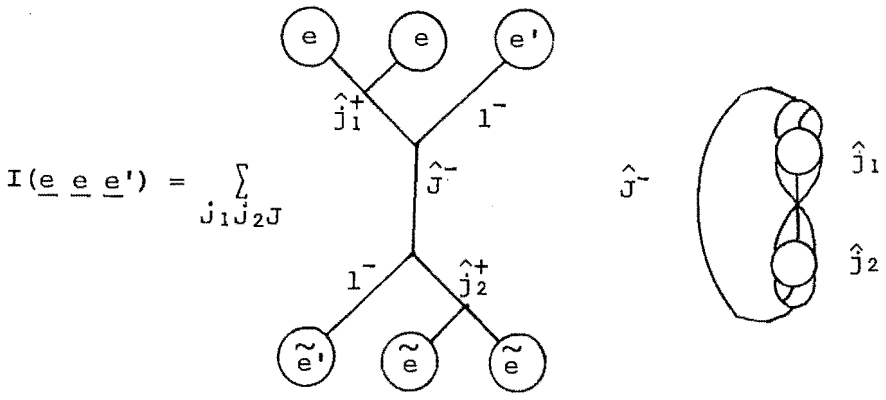
$R^{k\ell\ell'}_{\rho\sigma\tau}(\Omega)$ will be symmetric in the indices ρ,σ. Christie and Lockwood (1971) discuss the symmetries of general third and fourth rank tensors.

As in the two photon case we couple the polarisation vectors to angular momenta J. Pictorially we can express the intensity as in equation (4.2)



(4.2)

We consider the case of orientationally averaged scatterers and as in the last chapter we average over operations of the group and use the great orthogonality theorem to obtain equation 4.3.



(4.3)

Algebraically we have

$$I(\underline{e}\ \underline{e}\ \underline{e}') = \sum_{j_1 j_2 J} F_{J j_1 j_2}(\underline{e}\ \underline{e}\ \underline{e}') C_{J j_1 j_2}(\Omega) \tag{4.4}$$

where

$$F_{J j_1 j_2}(\underline{e}\ \underline{e}\ \underline{e}') = \sum_{\substack{\rho\rho'\sigma\sigma'\tau\tau' \\ m_1 m_2 M}} \begin{pmatrix} 1 & 1 & j_1 \\ \rho & \sigma & -m_1 \end{pmatrix} \begin{pmatrix} 1 & 1 & j_2 \\ \rho' & \sigma' & -m_2 \end{pmatrix}$$

$$\begin{pmatrix} j_1 & 1 & J \\ m_1 & \tau & M \end{pmatrix} \begin{pmatrix} j_2 & 1 & J \\ m_2 & \tau' & M \end{pmatrix} \hat{j}_1 \hat{j}_2 \hat{J}\ e_\rho \tilde{e}_\rho,\ e_\sigma \tilde{e}_\sigma,\ e_\tau' \tilde{e}_\tau', \tag{4.5}$$

The constants have the form

$$C_{J j_1 j_2}(\Omega) = \sum_M R_{j_1 JM}(\Omega)\ R^*_{j_2 JM}(\Omega)\ \hat{j}_1 \hat{j}_2 \hat{J}$$

where

$$R_{j_1 JM}(\Omega) = \sum_{\rho\sigma\tau m_1} \begin{pmatrix} 1 & 1 & j_1 \\ \rho & \sigma & -m_1 \end{pmatrix} \begin{pmatrix} j_1 & 1 & J \\ m_1 & \tau & -M \end{pmatrix} R_{\rho\sigma\tau}(\Omega) \tag{4.6}$$

Equations 4.3 and 4.4 are the analogues of equations 3.35, 3.36 for the two photon case where we express the intensity as a product of geometrical factors and physical constants. There are six independent geometrical factors $F_{J j_1 j_2}(\underline{e}\ \underline{e}\ \underline{e}')$

$$F_{100}$$
$$F_{102}^{+} = (F_{102} + F_{120})/\sqrt{2}$$
$$F_{102}^{-} = i(F_{102} - F_{120})/\sqrt{2}$$
$$F_{122}$$
$$F_{222}$$
$$F_{322} \tag{4.6}$$

j_1, j_2 are restricted to the values 0,2 for the case where $e_1 = e_2$ as the antisymmetric coupling $[\underline{e}_1\ \underline{e}_2]^{j=1}$ will be zero for identical incident photons. We choose to take the real combinations $F_{102\pm}$ of the complex conjugate terms F_{102} and F_{120}. The term $F_{102-}(\underline{e}\ \underline{e}\ \underline{e}')$ will be zero if we have the symmetry

$$I(\underline{e}\ \underline{e}\ \underline{e}') = I(\tilde{\underline{e}}\ \tilde{\underline{e}}\ \tilde{\underline{e}}') \tag{4.7}$$

(cf 2.11 for two photons). This symmetry will hold for electric dipole couplings in the absence of external magnetic fields but will not be true in general. It will however always hold for linear polarisations of the radiation beams. Andrews et al assume this symmetry by not distinguishing their terms ${}^{1A}\beta\ {}^{1B}\beta$ and ${}^{1B}\beta\ {}^{1A}\beta$. We see that we have one rank 2 term, one rank 3 term and four rank 1 terms distinguished unambiguously by the couplings to the angular momenta j_1 and j_2. This is preferable to the work of Andrews et al who make an arbitrary distinction for the three rank 1 terms.

We now wish to express the factors $F_{Jj_1j_2}$ in terms of scalar products as in the two photon case. We can use the results from the last chapter for the rank 1 terms however the rank 2 and 3 terms are more difficult. Minard, Stedman and McLellan (to be published) give a full analysis of geometrical factors for both three and four photon processes and we use their results here,

$$F_{100} = \frac{1}{3\sqrt{3}} |\underline{e}\cdot\underline{e}|^2$$

$$F_{102+} = \frac{2}{3\sqrt{30}} [3h_1 - |\underline{e}\cdot\underline{e}|^2]$$

$$F_{102-} = \frac{2}{\sqrt{30}} h_2$$

$$F_{122} = \frac{1}{15\sqrt{3}} [9|\underline{e}\cdot\underline{e}'|^2 - 6h_1 + |\underline{e}\cdot\underline{e}|^2]$$

$$F_{222} = \frac{1}{3\sqrt{5}} [2 - |\underline{e}\cdot\underline{e}|^2 - |\underline{e}\cdot\underline{e}'|^2 - 2|\underline{e}\cdot\underline{e}'^*|^2 + 2h_1]$$

$$F_{322} = \frac{1}{15\sqrt{7}} [5 + 10|\underline{e}\cdot\underline{e}'^*|^2 - 4|\underline{e}\cdot\underline{e}'|^2 - |\underline{e}\cdot\underline{e}|^2 - 4h_1] \quad (4.8)$$

where

$$h_1 = \mathrm{Re}[(\underline{e}\cdot\underline{e})(\underline{e}'\cdot\underline{e}^*)(\underline{e}^*\cdot\underline{e}'^*)], \quad h_2 = \mathrm{Im}[(\underline{e}\cdot\underline{e})(e'\cdot e^*)(\underline{e}^*\cdot\underline{e}'^*)]$$

These values for the geometrical factors when inserted into the expression for the intensity give a result which is in broad agreement with Andrews et al. They, however, assume no contribution from the term F_{102-} and they make a different separation of rank 1 terms. We see that in general the intensity is a function of the five parameters $(\underline{e}\cdot\underline{e})$, $(\underline{e}\cdot\underline{e}')$, $(\underline{e}\cdot\underline{e}'^*)$, h_1 and h_2. To determine the six constants $C_{Jj_1j_2}$ one requires six independent intensity measurements. For the case where F_{102-} is zero Andrews et al suggest the five intensity measurements ($I(\underline{e}\ \underline{e}') \equiv I(\underline{e}\ \underline{e}\ \underline{e}')$)

$$I(XX);\ I(XZ);\ I(RR);\ I(RL);\ I(RZ)$$

where X = (1,0,0), Z = (0,0,1), R = $(1,i,0)/\sqrt{2}$, L = $(1,-i,0)/\sqrt{2}$. For the general case where $F_{102-} \neq 0$ we require a sixth set of polarisation vectors ($\underline{e}$ $\underline{e}'$) such that $(\underline{e}\cdot\underline{e})(\underline{e}'\cdot\underline{e}^*)(\underline{e}^*\cdot\underline{e}^{*\prime})$ is a complex quantity. This cannot be achieved with the Stokes polarisation vectors we used in the two photon case (figure 2.2). The simplest type of polarisation vectors which will fulfill this requirement have the form.

$$\underline{e} \propto (1+i, -1, 0), \quad \underline{e}' \propto (1,i,0). \tag{4.9}$$

We can evaluate the intensity for the polarisation choices given above from equations 4.4 and 4.8. We then solve for the constants $c_{Jj_1j_2}$ to find

$$c_{322} = \sqrt{7}\ I(R\ R)$$

$$c_{222} = \frac{\sqrt{5}}{2}\ [3I(R\ Z) - I(R\ R)]$$

$$c_{122} = \frac{1}{2\sqrt{3}}\ [10I(R\ L) - 5I(R\ Z) + I(R\ R)]$$

$$c_{100} = \frac{1}{\sqrt{3}}\ [9I(X\ Z) - I(R\ R) - I(R\ L) - 4I(R\ Z)]$$

$$c_{102+} = \frac{3}{4\sqrt{30}}\ [30I(X\ X) - 30I(X\ Z) - 11I(R\ R) - 20I(R\ L) + 25I(R\ Z)] \tag{4.10}$$

The sixth constant C_{102-} will be a linear combination of all six intensity measurements and will depend on the form chosen for the sixth set of polarisation vectors (equation 4.9).

(b) Selection rules

As in the two photon case we can find which constants $C_{Jj_1j_2}$ will contribute for particular electronic ground states and phonon modes. Andrews et al give selection rules for higher symmetry groups and we generalise their results to apply to degenerate electronic ground states for all the point groups.

The tensors $R^{k\ell\ell'}_{\rho\sigma\tau}(\Omega)$ have the form

$$R^{k\ell\ell'}_{\rho\sigma\tau}(\Omega) \propto \langle\overline{\Lambda\ell'}|p'_\rho p'_\sigma p'_\tau V^\kappa_k|\Lambda\ell\rangle + 23 \text{ terms} \qquad (4.11)$$

Christie and Lockwood (1970) give all 24 terms with their appropriate denominators. Once again we can couple the operators together and use the Wigner Eckart theorem to give

$$R^{k\ell\ell'}_{\rho\sigma\tau}(\Omega) = \sum_{\substack{j_1Jm_1M\\ \mu n}} \begin{pmatrix} 1^- & 1^- & j_1^+ \\ \rho & \sigma & -m_1 \end{pmatrix} \begin{pmatrix} j_1^+ & 1^- & J^- \\ m_1 & \tau & -M \end{pmatrix} \begin{pmatrix} J^- & \kappa^* & \mu^* \\ M & k^* & n^* \end{pmatrix} \begin{pmatrix} \Lambda & \mu & \Lambda \\ \ell & n & \ell' \end{pmatrix} f_{j_1J\mu}(\Lambda,\kappa,\Omega) \qquad (4.12)$$

where we have used a reducible 3JM defined as

$$\begin{pmatrix} J^- & \kappa & \mu \\ M & k & n \end{pmatrix} = \sum_{\lambda\ell} \begin{pmatrix} \lambda & \kappa & \mu \\ \ell & k & n \end{pmatrix} \langle J^-\lambda\ell|J^-M\rangle \qquad (4.13)$$

Hence for the tensors $R^{k\ell\ell'}_{\rho\sigma\tau}(\Omega)$ to be non zero, J^- must reduce to λ in the point group under consideration and λ must obey

$$\lambda \in \Lambda \times \Lambda \times \kappa \qquad (4.14)$$

We can therefore find which values of J and so which $C_{Jj_1j_2}$ will contribute for any choice of Λ and κ. We list these values of J in table 14. Because we are coupling three polar vectors which transform as angular momenta $J = 1^-$ the resultant value of J will also be a polar vector (rather than an axial vector as in the two photon case). This means we can no longer consider the isomorphic groups together as groups containing reflections or inversions have different transformation properties when branching from J^+ and J^-.

A comparison of tables 13 and 14 will indicate which phonon modes can be activated by both the Raman and hyper Raman processes. Groups containing an inversion will never have phonon modes activated by both processes as the Raman effect activates only *gerade* modes, $\lambda^+(X_g)$, while the hyper Raman effect activates only *ungerade* modes $\lambda^-(X_u)$. Modes such as $\kappa = 0,1,2(A_1,E_1,E_2)$ of D_6 for singlet electronic states are activated by both effects whereas $\kappa = 3,\tilde{3}(B_1,B_2)$ are only activated by the hyper Raman process. Andrews et al give several specific examples in their paper.

4.2 C.A.R.S.

In this section we wish to indicate briefly how our analysis may be extended to the case of C.A.R.S. (coherent anti Stokes Raman scattering). Yuratich and Hanna (1976) have also examined this process using tensorial techniques.

C.A.R.S. and the related effect C.S.R.S. (coherent Stokes Raman scattering) are four photon processes involving two incident and two scattered photons. We find that it is possible to consider symmetries where we exchange incident and scattered photons as in the two photon case. This type of symmetry was not possible for the hyper Raman effect where the numbers of incident and scattered photons were different.

C.A.R.S. involves two identical incident photons with polarisation vectors $\underline{e}_1$ and frequency ω_1. A second laser beam is used to stimulate emission of a photon $\underline{e}_2^*$ with frequency $\omega_2 = \omega_1 \mp \omega_K$ where ω_K is a phonon frequency. A fourth photon $\underline{e}_3^*$ is then observed with a frequency $\omega_3 = 2\omega_1 - \omega_2$. The process is summarised in figure 4.1.

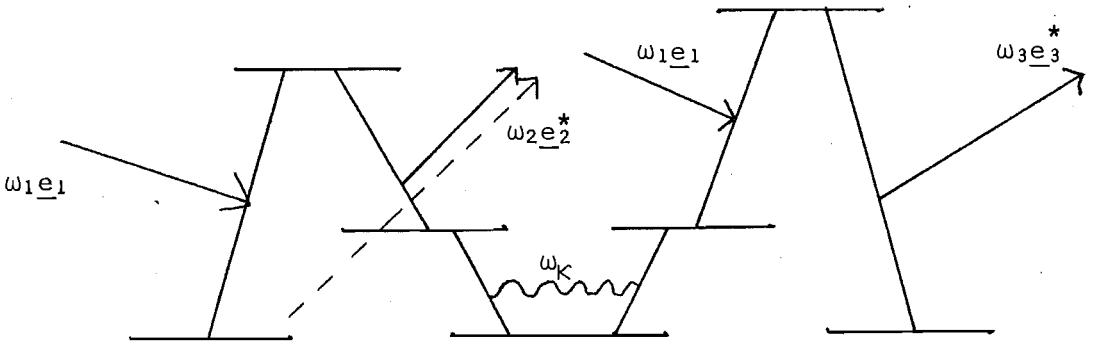


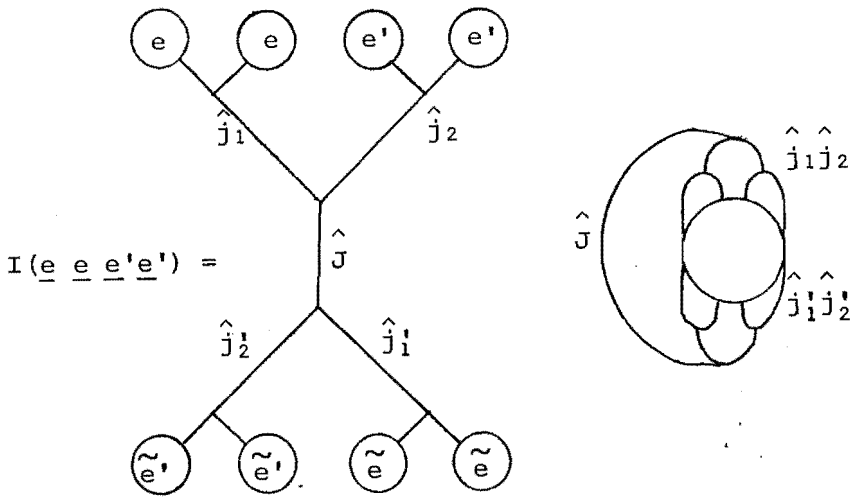
Figure 4.1: C.A.R.S. process.

We consider observing a scattered photon $\underline{e}_3^*$ such that $\underline{e}_3 = \underline{e}_2 \equiv \underline{e}'$. For the non resonant case (where we do not excite real electronic transitions) it is reasonable to approximate $\omega_1 = \omega_2 = \omega_3$ as for the vibrational Raman effect. This will allow the symmetry

$$I(\underline{e}\ \underline{e}\ \underline{e}'\underline{e}') = I(\underline{e}'\ \underline{e}'\ \underline{e}\ \underline{e}) \qquad (4.15)$$

where $\underline{e} \equiv \underline{e}_1$.

For the case of orientationally averaged scatterers we couple the polarisation vectors to angular momenta J as for the Raman and hyper Raman processes. The intensity can be expressed pictorially as in the diagram.



Algebraically we have

$$I(\underline{e}\ \underline{e}\ \underline{e}'\underline{e}') = \sum_{j_1 j_2 j'_1 j'_2 J} F_{J j_1 j_2 j'_1 j'_2}(\underline{e}\ \underline{e}\ \underline{e}'\underline{e}')\ C_{J j_1 j_2 j'_1 j'_2}(\Omega) \tag{4.16}$$

Obviously $j_1 j'_1 j_2$ and j'_2 must be even as antisymmetric products of $\underline{e} \otimes \underline{e}$ and $\underline{e}' \otimes \underline{e}'$ will disappear. The symmetry of equation 4.15 gives us the further restriction that $\{j_1 j_2 J\} = +1$ and so J must also be even. This leaves us with 14 non zero geometrical factors with the values J given in figure 4.2.

J	j_1	j_2	j_1'	j_2'	
0	0	0	0	0	
0	0	0	2	2	$\pm$
0	2	2	2	2	
2	0	2	0	2	
2	2	0	2	0	
2	0	2	2	0	$\pm$
2	0	2	2	2	$\pm$
2	2	0	2	2	$\pm$
2	2	2	2	2	
4	2	2	2	2	

Figure 4.2: Values of $Jj_1j_2j_1'j_2'$ contributing to non resonant C.A.R.S. ($e_2 = e_3$).

We choose real combinations of geometrical factors and define

$$F_{Jj_1j_2j_1'j_2'^{\pm}} = \frac{\theta_{\pm}}{\sqrt{2}} \left(F_{Jj_1j_2j_1'j_2'} \pm F_{Jj_1'j_2'j_1j_2}\right) \tag{4.17}$$

where $\theta_{\pm} = 1(i)$.

As in the hyper Raman case the factors $F_{Jj_1j_2j_1'j_2'}$- will not contribute if we have the additional symmetry

$$I(\underline{e}\ \underline{e}\ \underline{e}'\ \underline{e}') = I(\tilde{\underline{e}}\ \tilde{\underline{e}}\ \tilde{\underline{e}}'\ \tilde{\underline{e}}') \tag{4.18}$$

For this case the number of independent factors will be

reduced to 10. This symmetry will not be true in general. It will break down if we include interference between electric and magnetic dipole couplings or if we include a time reversal odd interaction (e.g. an external magnetic field).

As for the two and three photon cases the geometrical factors can be expressed in terms of scalar products of the polarisation vectors. Minard, Stedman and McLellan (to be published) have performed this reduction for a general four photon interaction. Using their results we find for the case where $\underline{e}_2 = \underline{e}_3 \equiv \underline{e}'$ that the intensity is a function of 12 independent geometrical parameters (compared with 2 for Raman and 5 for hyper Raman scattering). The 12 parameters are

$$|\underline{e}\cdot\underline{e}'|^4;\ |\underline{e}'\cdot\underline{e}^*|^4;\ (\underline{e}\cdot\underline{e})^*(\underline{e}'\cdot\underline{e}') \pm \text{c.c.};$$

$$(\underline{e}\cdot\underline{e})^2(\underline{e}\cdot\underline{e})^*(\underline{e}'\cdot\underline{e}')^* \pm \text{c.c.};\ (\underline{e}^*\cdot\underline{e}')^2(\underline{e}'\cdot\underline{e}')^*(\underline{e}\cdot\underline{e}) \pm \text{c.c.};$$

$$(\underline{e}\cdot\underline{e})(\underline{e}'\cdot\underline{e}^*)(\underline{e}\cdot\underline{e}')^* \pm \text{c.c.};\ (\underline{e}'\cdot\underline{e}')^*(\underline{e}\cdot\underline{e}')(\underline{e}'\cdot\underline{e}^*) \pm \text{c.c.};$$

This is the largest number of independent parameters one can obtain from two polarisation vectors $\underline{e},\underline{e}'$ as only 12 constants are involved (3 complex components each). For the more general case where $\underline{e}_2 \neq \underline{e}_3$ there will be additional geometrical factors as we will no longer be restricted to j_2, j_2', and J being even.

As for the Raman and hyper Raman effects it is possible to determine selection rules for various electron and phonon

symmetries. For the general case we require $\mu = \Lambda \times \Lambda \times \kappa$ to branch from $J = 0^+, 1^+, 2^+, 3^+, 4^+$ which is similar to the hyper Raman selection rule (equation 4.14) although now we have J^+ rather than J^-. When we consider the non resonant case with the condition $\underline{e}_2 = \underline{e}_3$ we are restricted to $J = 0^+, 2^+, 4^+$. The extra symmetry condition (equation 4.15) which applies in this case will impose greater restrictions on the possible values of μ, in a manner similar to that which occurred for the non resonant Raman effect. This will further reduce the number of independent spectra $C_{Jj_1j_2j_1'j_2'}(\Omega)$ which will contribute in a particular situation.

The preceding sections indicate how the techniques developed in chapter two may be extended in order to examine non linear processes. Diagram techniques provide an efficient method for determining the polarisation dependence of the intensity. We find that the coupling of polarisation vectors to angular momenta J provides an unambiguous separation of the geometrical factors. This is preferable to the arbitrary separation of rank 1 terms performed by Andrews et al for the hyper Raman effect. We also generalise these authors by allowing for a contribution to the intensity from a time reversal odd interaction or from a magnetic dipole coupling. A similar analysis can be carried out for the C.A.R.S. effect. For this case we also consider the extra symmetries which can result from the equal numbers of incident and scattered photons.

CHAPTER FIVE

NATURAL AND INDUCED OPTICAL ACTIVITY

The formalism of chapter two is readily applied to an examination of optical activity. We examine in detail natural and induced circular dichroism.

Circular dichroism (C.D.) is the differential absorption of right and left handed circularly polarised light. This effect occurs naturally in molecules or crystals where the symmetry corresponds to one of the chiral point groups (C_n,D_n,O,T,K). It may also be induced in non chiral groups. The most well known method of inducing circular dichroism is by an external magnetic field (M.C.D.). Recent workers have used group theoretical approaches to analyse the symmetry properties of these effects (e.g. Dobosh 1974, Manson et al 1977, Piepho and Schatz.) One can also induce circular dichroism by applying an external electric field (E.C.D.) (e.g. Schipper 1978) or by coupling to the vibrations of the crystal or molecules (V.C.D.)(e.g. Craig et al 1976, 1977, Nafie et al 1977). More recently similar effects have been studied for two photon processes e.g. Raman and Rayleigh optical activity (e.g. Barron 1979, Barron and Buckingham 1975, Barron and Nørby Svendson 1980) where one looks for differences in the scattering intensity for right and left circularly polarised incident light.

In this chapter we use a group theoretical formalism analogous to that detailed in chapter two to analyse the

symmetry properties of handed absorption effects. We consider two couplings: pure electric dipole coupling (E.D - E.D coupling) and the interference between electric and magnetic dipole terms (E.D - M.D coupling). We also consider applying external magnetic and electric fields to these two cases.

5.1 ELECTRIC DIPOLE - ELECTRIC DIPOLE COUPLING

The expression for the intensity of a one photon absorption process analogous to equation 2.13 is

$$I(\underline{e}) = \sum_{\alpha} F_{\alpha}(\underline{e}) c_{\alpha}(\Omega) \tag{5.1}$$

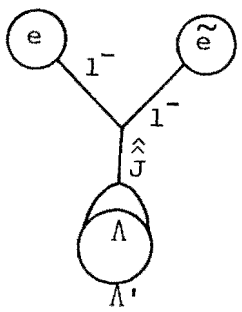
For electric dipole coupling in a spherical basis $\alpha \equiv JM$ we have

$$F_{JM}(\underline{e}) = \sum_{\rho\rho'} e_{\rho} \tilde{e}_{\rho'} \begin{pmatrix} 1 & 1 & J \\ \rho & \rho' & M \end{pmatrix} \hat{J} \tag{5.2}$$

$$c_{JM}(\Omega) \propto \sum_{\ell\ell'\rho\rho'} \langle \Lambda' \overline{\ell}' | p_{\rho} | \Lambda \ell \rangle \langle \Lambda' \overline{\ell}' | p_{\rho'} | \Lambda \ell \rangle^{*} \begin{pmatrix} 1 & 1 & J \\ \rho & \rho' & M \end{pmatrix} \hat{J} \tag{5.3}$$

where Λ, Λ' are the symmetries of the ground and final electronic states. The intensity in this basis can be expressed diagrammatically as in equation 5.4.

$$I(\underline{e}) = \sum_{J}$$



(5.4)

For circular dichroism we require the absorption for right (e_R) and left (e_L) circularly polarised light to be different

$$I(\underline{e}_R) - I(\underline{e}_L) \neq 0 \tag{5.5}$$

Using equations 5.1 - 5.3 and since $\tilde{e}_R = e_L$ (appendix A1) we have

$$I(\underline{e}_R) - I(\underline{e}_L) = \sum_{JM\rho\rho'} e_\rho \tilde{e}_{\rho'} \hat{J}\, c_{JM}(\Omega) \left| \begin{pmatrix} 1^- & 1^- & J \\ \rho & \rho' & M \end{pmatrix} - \begin{pmatrix} 1^- & 1^- & J \\ \rho' & \rho & M \end{pmatrix} \right| \tag{5.6}$$

It is clear that only the antisymmetric coupling to angular momentum $J = 1^+$ will survive i.e.

$$I(\underline{e}_R) - I(\underline{e}_L) = \sum_{M\rho\rho'} 2\, e_\rho \tilde{e}_{\rho'} \hat{1}\, c_{1M}(\Omega) \begin{pmatrix} 1^- & 1^- & 1^+ \\ \rho & \rho & M \end{pmatrix} \tag{5.7}$$

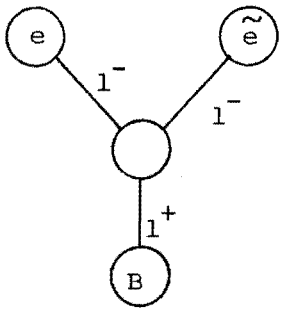
We have however the further restriction that the intensity is a real quantity. On complex conjugating equation 5.7 we find that the expression is only real if $c(\Omega) = -c(\Omega)^*$ i.e. the physical constant is imaginary. It is clear from equation 5.3 that $c(\Omega)$ is real (the electric dipole interactions are time reversal even (appendix A1)). As this $J = 1^+$ term is also forbidden we will not observe any differential absorption of right and left handed circularly polarised light for this case.

To induce C.D. it is necessary to make the kernal $c(\Omega)$ imaginary. This can be done by introducing a time reversal odd interaction. An obvious candidate is the magnetic field.

(a) Magnetic Circular Dichroism

We wish to include the magnetic field interaction an odd number of times so that the time reversal signatures do not cancel. We consider only the first order or linear coupling to the magnetic field. The intensity can be expressed pictorially or algebraically as

$I(\underline{e},\underline{B})$ =



or

$$I(\underline{e}\ \underline{B}) = \sum_{\rho\sigma\tau} e_\rho \tilde{e}_\sigma B_\tau\ c_{\rho\sigma\tau}(\underline{B}\ \Omega) \qquad (5.8)$$

The expression for the constant now has the form (in a cartesian basis

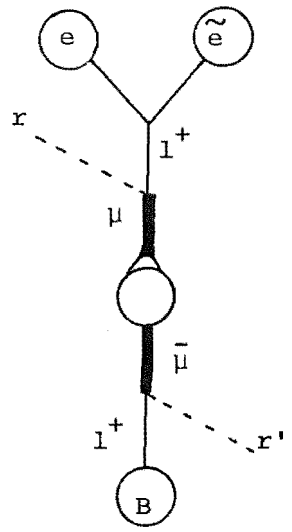
$$c_{\rho\sigma\tau}(\underline{B}\Omega) \propto \sum \langle\Lambda'\ell'|B^e_\tau|\alpha\rangle\langle\alpha|p_\rho|\Lambda\ell\rangle\langle\Lambda'\ell'|p_\sigma|\Lambda\ell\rangle^* + \ldots \qquad (5.9)$$

where B^e is the electronic part of the magnetic field operator. There will be other similar terms corresponding to different orderings of the operators. As $\underline{B}$ is time reversal odd we now have that $c(\underline{B}\ \Omega) = -c^*(\underline{B}\Omega)$ as required.

We find it useful to couple the photon operators to angular momentum J, as before, and then to branch to a

representation of the point group as in equation 5.10. (The solid line represent a transformation to a point group and the dashed lines the branching multiplicity)

$$I(\underline{e}\ \underline{B}) = \sum_{\mu\bar{\mu}rr'} \tag{5.10}$$



As in §2.3c we can average over the operations of the point group and use the great orthogonality theorem to show that $\mu = \bar{\mu}$. After averaging over the point group the intensity will have the form

$$I(\underline{e}\ \underline{B}) = \sum_{\mu rr'} F_{\mu rr'}(\underline{e}\ \underline{B})\ c_{\mu rr'}(\Omega\ \underline{B}) \tag{5.11}$$

where

$$F_{\mu rr'}(\underline{e}\ \underline{B}) = \sum_{\rho\sigma\tau} e_{\rho}^{1^-}\tilde{e}_{\sigma}^{1^-} \langle 1^-\rho, 1^-\sigma | \mu nr\rangle\langle \mu nr' | 1^+\tau\rangle B_{\tau}^{1^+} \tag{5.12}$$

The reducible coupling coefficients are defined in equation 2.33 and both these and the transformation coefficients can be found in table 2.

To observe the differential absorption of right and left circularly polarised light we have shown (equations

5.6, 5.7) that only the antisymmetric coupling of $\underline{e},\underline{\tilde{e}}$ to angular momentum $J = 1^+$ will survive. This means that both μ_r and $\mu_{r'}$ must branch from $J = 1^+$. We can use this fact and equation (5.12) to find the geometrical factors $F_{\mu rr'}(\underline{e}\ \underline{B})$ which will contribute to the intensity. As in chapter two we prefer to deal with real geometrical factors and physical constants. We have that

$$F^*_{\mu rr'}(\underline{e}\ \underline{B}) = \varepsilon^{\mu}_{r}\varepsilon^{\mu}_{r'}\{11\mu r\}\ F_{\mu^* rr'}\ (\underline{e}\ \underline{B}) \tag{5.13}$$

and we define real geometrical factors

$$F_{\mu rr'\pm} = \frac{\theta_{\pm}}{g}\ (F_{\mu rr'} \pm F^*_{\mu rr'}) \tag{5.14}$$

where $\theta_{\pm} = 1(i)$ and $g = 2$ if $\mu = \mu^*$ and $\sqrt{2}$ otherwise.

As an example we consider the case of orientationally averaged molecules where the symmetry group is R_3. In this case μ is confined to the value $\mu = 1^+$ with no multiplicities. Using equation 5.12 and Table 2 we find that we have

$$\begin{aligned} F_{100}(\underline{e}\ \underline{B}) &= -\frac{1}{\sqrt{2}}\ [(e_x\tilde{e}_y - e_y\tilde{e}_x)B_z + (e_y\tilde{e}_z - e_z\tilde{e}_y)B_x \\ &\quad + (e_z e_x - e_x e_z)B_y \\ &= \frac{-1}{\sqrt{2}}\ (\underline{e} \times \underline{\tilde{e}})\cdot\underline{B} \end{aligned} \tag{5.15}$$

For circularly polarised light i.e. $\underline{e} = \frac{1}{\sqrt{2}}(1,i,0)$, $\underline{e} \times \underline{\tilde{e}} = (0,0,1) = \underline{k}$ where $\underline{k}$ is the direction of the propagation of the light beam. To observe M.C.D. in powders or fluids

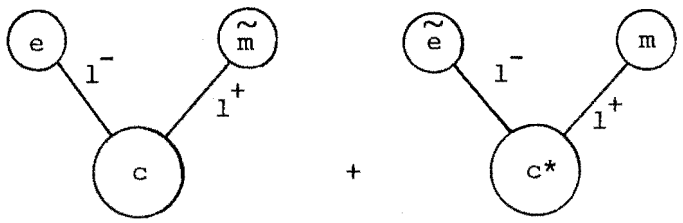
there must be a component of $\underline{B}$ parallel to the direction of the light beam so that $F_{100} \propto \underline{k}\cdot\underline{B} \neq 0$. This result is well known. For the groups K, O, O_h, T, T_h, T_d we have once again that μ is confined to one value, $\mu=1$, with no multiplicities and we find that equation 5.15 is true for these groups also. For these high symmetry groups the geometrical factors depend only on the relative orientations of $\underline{k}$ and $\underline{B}$ and so the crystal orientation is unimportant. In these systems the linear M.C.D. spectrum is said to be isotropic. This result has been proved only recently (Manson et al 1977).

We tabulate the non-zero geometrical factors for all the point groups in table 15. We note that for the groups D_6, D_4, D_3 and those isomorphic to them we have two geometrical factors $F_1 \propto k_z B_z$, $F_2 \propto k_x B_x + k_y B_y$. The dependence on x and y is symmetrical and therefore the spectrum is axially symmetric for these groups. This means the crystal can be rotated about the z axis without altering the M.C.D. spectrum. This is a new result.

5.2 ELECTRIC DIPOLE - MAGNETIC DIPOLE COUPLING

The interference between electric and magnetic dipole coupling involves two complex conjugate terms. Diagrammatically we have

$I(\underline{e})$ =



(5.16)

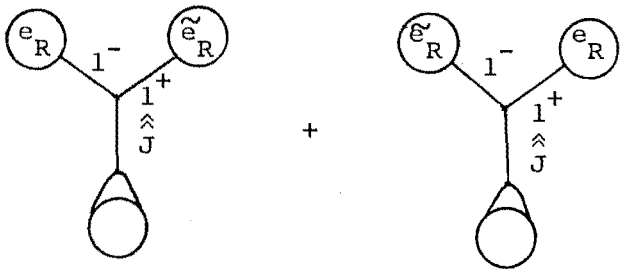
The physical constant has the form

$$c_{\rho\sigma}(\Omega) = \sum_{\ell\ell'} \langle \Lambda'\bar{\ell}'|p_\rho|\Lambda\ell\rangle\langle\Lambda\bar{\ell}'|L_\sigma|\Lambda\ell\rangle^* \qquad (5.17)$$

Where $\underline{L}$ is the angular momentum of the electron. As both the electric and magnetic dipole interaction terms have the same time reversal properties (appendix A1), we can see from equation 5.17 that $c(\Omega) = c^*(\Omega)$.

Once again we can couple to angular momenta J. As we are now coupling an axial ($\underline{m}$) and a polar ($\underline{e}$) vector J will be odd under inversion i.e. J^-. From appendix A1 we have that $\tilde{e}_R = e_L$ and $\tilde{m}_R = -m_L$. For right circularly polarised light (i.e. $\underline{e}_R = (1,i,0)/\sqrt{2}$ and $\underline{k} = (0,0,1)$) we have from the definition $\underline{m} = i\underline{e} \times \underline{k}$ that $\underline{m}_R = -\underline{e}_R$. Similarly $m_L = +\underline{e}_L$. The intensity difference for the absorption of right and left circularly polarised light can then be expressed as in equation 5.18

$$I(\underline{e}_R) - I(\underline{e}_L) = \qquad (5.18)$$



Only the symmetric terms $J = 0^-, 2^-$ will survive and in this case the intensity is real as required.

If we impose a point group symmetry then, as in §2.3b, J must branch to the identity irrep of the point group. i.e. $J = 0^-, 2^- \rightarrow \mu = 0$. this is true for the chiral groups (C_n, D_n, O, T, K). The absence of inversions and reflections means that J^+ and J^- transform identically and so $J = 0^- \rightarrow \mu = 0$ in these groups. It is well known that natural optical activity occurs in crystals and molecules with these symmetries. Our analysis however also permits the preferential absorption of right and left circularly polarised light if the identity irrep of the point group branches from $J = 2^-$. We find that this is also possible in the achiral groups D_{2d}, C_{2v}, C_s and S_4. We see no reason not to include the $J = 2^-$ terms and so we would expect these groups to exhibit natural circular dichroism. This also appears to be a new result.

Upon orientationally averaging i.e. in fluids or powders we require invariance under the full rotation group O_3 as well. This restricts us to $J = 0^-$. In this case we only expect molecules with the symmetry of one of the chiral groups to exhibit natural optical activity.

It is also possible to induce optical activity in other groups. As the intensity must remain real we are only permitted the addition of a time reversal even interaction. We consider a linear interaction with an electric field.

(a) Electric circular dichroism

The interaction with the electric field can be treated in the same manner as the interaction with the magnetic field in the previous section. The equations analogous to 5.11 and 5.12 are

$$I(\underline{e}\ \underline{E}) = \sum_{\mu rr'} F_{\mu rr'}\ (\underline{e}\ \underline{E})\ c_{\mu rr'}(\Omega \underline{E}) \qquad (5.19)$$

where

$$F_{\mu rr'}(\underline{eE}) = \sum_{\rho\sigma\tau} e_{\rho}^{1^-}\ \tilde{m}_{\sigma}^{1^+}\ \langle 1^-\rho,1^+\sigma|\mu nr\rangle\langle\mu nr'|1^-\tau\rangle E_{\tau}^{1^-} \qquad (5.20)$$

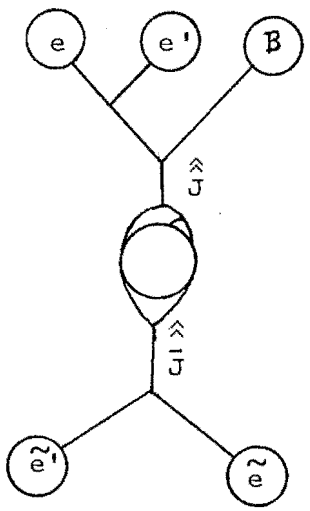
where now the electric field transforms as a polar vector. We now require that μ_r branches from $J = 0^-$ or 2^- and that $\mu_{r'}$ branches from $J = 1^-$. This is never true for the high symmetry groups R_3,K,O,O_h,T_d so that E.C.D. is forbidden for these symmetries. This agrees with the result of Schipper that E.C.D. will not occur in rotationally averaged systems. We give the forms of the non zero geometrical factors $F_{\mu rr'}(\underline{e}\ \underline{E})$ for other groups in table 16. We find that E.C.D. can be exhibited by all groups other than the high symmetry groups noted above. For the groups T and T_h the spectrum is isotropic while for the groups D_6, D_4 and those isomorphic to them the spectrum is axially symmetric.

Schipper gives a selection rule for the special case of the electric field constrained to be along the propagation direction of the radiation beams. However he only includes values of $e_{\rho}\ \tilde{m}_{\sigma}$ where $\rho = \sigma$. We see no

reason for not including all values for ρ and σ in equation 5.20.

It is obvious from the preceeding sections that a great deal of information can be obtained from the group theoretical techniques we have been using. New results such as the axial symmetry of the E.C.D. and M.C.D. spectra for certain point groups were immediately apparent. It would not be difficult to extend this analysis to the two photon case e.g. Raman optical activity. For natural optical activity the analysis would be similar to section 5.2 except the intensity will be quartic in the polarisation vectors and there will be four interference terms in the analogue of equation 5.16. For the induced handed effects the intensity could be expressed as in the diagram

$I(\underline{e}\ \underline{e}'\underline{B})$ =



Induced Raman optical activity

Selection rules could be derived from here in a manner similar to that for M.C.D. or E.C.D.

CHAPTER SIX

CONCLUSION

We have developed a concise and rigorous method for analysing the symmetry properties of a wide variety of spectroscopic processes. The group theoretical techniques employed have produced several new results and generalised previous work.

The results of chapter two together with the appropriate tables provide a method for determining the parameters of a scattering intensity from a set of independent experimental arrangements. It is hoped that these results will enable the efficient extraction of information from polarisation experiments. The relationships among the intensity measurements (table 11) may help in determining the symmetry of the scatterer.

It is expected that the selection rules for the vibrational Raman effect will be useful in a variety of systems (e.g. those with Kramers degeneracy). More sensitive experiments may uncover further cases where the degeneracy of the electronic ground state causes additional contributions to the intensity (as in the results of Johnstone et al). In these cases the selection rules will facilitate the assignment of phonon modes and also the determination of the electronic symmetry. It is hoped that similar uses may be made of the hyper Raman selection rules. It would be useful to extend these results to resonant scattering.

The methods used to analyse natural and induced circular dichroism may be readily extended to a wide range of handed effects. In particular we hope to investigate the two photon effects such as Raman optical activity. The results obtained for M.C.D. and E.C.D. are open to easy experimental verification.

It is clear that these types of symmetry considerations can provide a great deal of information about a variety of spectroscopic processes.

APPENDICES

A1 TIME REVERSAL

Time reversal is an antilinear operation (Messiah (1961), Abragam and Bleaney (1970)). Under the time reversal operator κ_τ, states and operators go to their time reversed states (denoted by a bar) while all multiplying factors are complex conjugated e.g.

$$\kappa_\tau(a|b\rangle) = a^*|\bar{b}\rangle$$

$$\kappa_\tau 0 \kappa_\tau^\dagger = \bar{0} \qquad \text{(A1.1)}$$

For matrix elements we have the identity

$$\langle a|0|b\rangle = \langle\bar{b}|\bar{0}^\dagger|\bar{a}\rangle \qquad \text{(A1.2)}$$

where † denotes hermitian conjugation. We also have

$$\bar{0}^\dagger = \tau_0 0$$

$$|\overline{\Lambda\ell}\rangle = \tau_\Lambda|\Lambda\ell\rangle \qquad \text{(A1.3)}$$

where τ_0, $\tau_\Lambda = \pm 1$ are the time reversal signatures of the operator or state. The position and momentum operators are time reversal even ($\tau_0 = +1$) and odd ($\tau_0 = -1$) respectively. For electronic states $\tau_\Lambda = +1(-1)$ as the number of electrons is even(odd).

We can consider matrix elements between partners ℓ,ℓ' of a degenerate state Λ.

$$M_{\ell\ell'} = \langle\overline{\Lambda\ell}|0|\Lambda\ell'\rangle \qquad \text{(A1.4)}$$

Using (A1.2) we have that

$$M_{\ell\ell'} = \langle\overline{\Lambda\ell}'|\bar{0}^{\dagger}|\overline{\overline{\Lambda\ell}}\rangle$$

$$= \tau_0\tau_\Lambda M_{\ell'\ell} \qquad \text{(A1.5)}$$

and so the matrix is symmetric or antisymmetric as $\tau_0\tau_\Lambda = \pm 1$.

Stedman and Butler (1980) give a full analysis of the time reversal symmetries of tensor operators.

Application to Electromagnetic Radiation

Time reversal considerations can be applied to electromagnetic radiation and particularly in our case to its interaction with matter. The electric and magnetic field operators are time reversal even and odd respectively. We consider the electric vector potential $\underline{A}(\underline{r},t)$. We have that $\underline{E} = -\frac{d\underline{A}}{d-t}$ and so

$$\bar{\underline{A}}(\underline{r}t) = -\underline{A}(\underline{r}t) \qquad \text{(A 1.6)}$$

We can expand $\underline{A}$ in terms of plane waves and use its time reversal properties to explore the symmetries of the photon operators (see Stedman (to be published)).

$$\underline{A}(\underline{r}t) = \left(\frac{\hbar}{2\varepsilon_0 V\omega_k}\right)^{\frac{1}{2}} \sum_{\underline{k}j} \underline{e}_{\underline{k}j}\, e^{i(\underline{k}.\underline{r}-\omega t)}\, \hat{a}_{\underline{k}j} + \underline{e}^{*}_{\underline{k}j}\, e^{-i(\underline{k}.\underline{r}-\omega t)} \hat{a}^{\dagger}_{\underline{k}j}$$

Under time reversal this becomes

$$\underline{A}(\underline{r}t) = \left(\frac{\hbar}{2\varepsilon_o V\omega_k}\right)^{\frac{1}{2}} \sum_{\underline{k}j} \underline{e}^*_{\underline{k}j}\, e^{-i(\underline{k}.\underline{r}-\omega t)}\, \overline{\hat{a}_{\underline{k}j}} + hc$$

$$= -\underline{A}(\underline{r}t) \quad . \tag{A1.8}$$

$\hat{a}_{\underline{k}j}$ is the operator which annihilates state $|\underline{k}j\rangle$ and we associate $\overline{\hat{a}_{\underline{k}j}}$ with the annihilation of state $|\overline{\underline{k}j}\rangle$. We thus have

$$\overline{\hat{a}_{\underline{k}j}} = \hat{a}_{\overline{\underline{k}j}} \tag{A1.9}$$

Equating coefficients of $\hat{a}_{\underline{k}j}$ in the two parts of (A1.8) gives that

$$\underline{e}^*_{\underline{k}j} = -\underline{e}_{\overline{\underline{k}j}} \tag{A1.10}$$

Time reversal takes the wavevector $\underline{k}$ to $-\underline{k}$ so we have

$$\underline{e}^*_{\underline{k}} = -\underline{e}_{-\overline{k}j} \tag{A1.11}$$

The interaction of matter and radiation provides terms of the form $\underline{A}.\underline{p}$ where we can expand our expression for $\underline{A}$ to give

$$\underline{A}.\underline{p} = \left(\frac{\hbar}{2\varepsilon_o V\omega_k}\right)^{\frac{1}{2}} \sum_{\underline{k}j} \underline{p}.(\underline{e}_{\underline{k}j}\, \hat{a}_{\underline{k}j}(1 + i\underline{k}.\underline{r} + \ldots) + h.c.) \tag{A1.12}$$

The first term $\hat{a}_{\underline{k}j}\, \underline{p}.\underline{e}_{\underline{k}j}$ is the electric dipole term, the second $\hat{a}_{\underline{k}j}(\underline{p}.\underline{e}_{\underline{k}j})(\underline{k}.\underline{r})i$ can be expressed as the sum of two terms one of which is $\hat{a}_{\underline{k}j}(\underline{p}\times\underline{r})\; i(\underline{e}_{\underline{k}j} \times \underline{k})$ where $\underline{p} \times \underline{r}$

is the angular momentum $\underline{L}$ and $i\ \underline{e}_{\underline{k}j} \times \underline{k}$ is the magnetic dipole moment $\underline{M}_{\underline{k}j}$.

Using A(1.11) we have that

$$\begin{aligned} \underline{M}^{*}_{\underline{k}j} &= (i\ \underline{e}_{\underline{k}j} \times \underline{k})^{*} \\ &= -i\ \underline{e}_{-\underline{k}\bar{j}} \times -\underline{k} \\ &= -\ M_{\underline{k}\bar{j}} \end{aligned} \tag{A1.13}$$

We have therefore that the magnetic dipole operator behaves in the same way as the electric dipole operator. Both interactions are time reversal even as can be seen from the time reversal properties of the operators in equation (A1.12).

When we consider the handedness of the operators however their behaviour is distinct. We define right and left handed polarised light by

$$\begin{aligned} \underline{e}_{zR} &= \frac{1}{\sqrt{2}}\ (y - ix) \\ \underline{e}_{zL} &= \frac{1}{\sqrt{2}}\ (y + ix) \end{aligned} \tag{A1.14}$$

and so we have

$$\underline{e}^{*}_{zR} = \underline{e}_{zL} \tag{A1.15}$$

For the magnetic dipole operator we have from our definition of $\underline{M}$ and (A1.15) that

$$\underline{M}^{*}_{ZR} = -\underline{M}_{ZL} \qquad \text{(A1.16)}$$

It is this distinction that allows handed effects to result from the interference of magnetic and electric dipole terms (See chapter 5).

A2. GROUP THEORY

At all points in the text we use the notation and phase conventions of Butler (1981). The notation for the labelling of group irreps can be found in table 1 and we refer the reader to Butler for more general definitions. For the diagrammatic formulation of the group theoretical analysis we use the definitions and conventions of Stedman (1975). Here we wish to clarify some specific points referred to in the text.

Phases ε_r^μ

The Derome-Sharp lemma for complex conjugation of 3JM symbols can be expressed as

$$\begin{pmatrix} \lambda_1 & \lambda_2 & \lambda_3 \\ \ell_1 & \ell_2 & \ell_3 \end{pmatrix}_{r}^{*} = \sum_{r'} \begin{pmatrix} \lambda_1 \\ \ell_1 \end{pmatrix}^{*} \begin{pmatrix} \lambda_2 \\ \ell_2 \end{pmatrix}^{*} \begin{pmatrix} \lambda_3 \\ \ell_3 \end{pmatrix}^{*} \begin{pmatrix} \lambda_1^* & \lambda_2^* & \lambda_3^* \\ \ell_1^* & \ell_2^* & \ell_3^* \end{pmatrix}_{r'} A_{rr'} \qquad \text{(A2.1)}$$

We have defined reducible coupling coefficients as

$$\langle l\rho, l\rho' | Ja\lambda\ell \rangle = \sum_{mm'M} \langle l\rho | lm \rangle \langle l\rho' | lm' \rangle \langle lm, lm' | JM \rangle \langle JM | Ja\lambda\ell \rangle \qquad \text{(A2.2)}$$

We can apply the Derome-Sharp lemma to these coupling coefficients to obtain

$$\langle l\rho, l\rho' | Ja\lambda\ell \rangle^{*} = \sum_{J'a'} \langle l\rho, l\rho' | J'a'\lambda^*\ell^* \rangle \begin{pmatrix} \lambda \\ \ell \end{pmatrix}^{*} A_{Ja,J'a'} \qquad \text{(A2.3)}$$

where the 2JM's $\begin{Bmatrix} l \\ \rho \end{Bmatrix}$ for ρ in a cartesian basis are unity.

We relabel the parentages Ja → r, J'a' → r' and find from the orthogonality of the coefficients that

$$A_{rr'} = \sum_{\rho\rho'} \langle J'a'\lambda^*\ell^* | 1\rho, 1\rho' \rangle \langle Ja\lambda\ell | 1\rho, 1\rho' \rangle \begin{pmatrix} \lambda \\ \ell \end{pmatrix} \qquad \text{(A2.4)}$$

An examination of table 2 shows that $A_{rr'} = \pm \delta_{rr'}$. It is not possible to redefine the phases of any kets to make $A_{rr'} = +\delta_{rr'}$ and so we must include this phase in all our calculations. We refer to it as $\epsilon_r^\mu \equiv A_{rr}$ and tabulate its values for our choices of r in table 2.

Reality of $R^{k\ell\ell'}_{\rho\rho'}(R^{k\ell\ell'}_{\sigma\sigma'})^*$

We can define $R^{k\ell\ell'}_{\rho\rho'}$ as the matrix element of the coupled operators p^1, p^1 and V^K.

$$R^{k\ell\ell'}_{\rho\rho'} = \sum_{\substack{\mu m \nu n \\ rs}} \langle \overline{\Lambda\ell}' | [[p^1 p^1]^{\mu r} V^\kappa]^{\nu s}_m | \Lambda\ell \rangle$$

$$\langle 1\rho, 1\rho' | \mu n r \rangle \langle \mu n, \kappa k | \nu m s \rangle \qquad \text{(A2.5)}$$

To complex conjugate this expression we can use the Derome Sharp lemma (A2.1) for the coupling coefficients. For the matrix element we have from equation (A1.2)

$$\langle \overline{\Lambda\ell}' | [[p^1 p^1]^{\mu r} V^\kappa]^{\nu s}_n | \Lambda\ell \rangle^* = \langle \overline{\overline{\Lambda\ell}}' | [\overline{[p^1 p^1]^{\mu r} V^\kappa}]^{\nu s}_n | \overline{\Lambda\ell} \rangle \qquad \text{(A2.6)}$$

The time reversed coupled operators can be expanded as for example

$$\overline{[O^{\kappa}N^{\mu}]}_{n}^{\nu s} = \sum_{km} \overline{O_k^{\kappa}}\ \overline{N_m^{\mu}} \langle \kappa k, \mu m | s \nu n \rangle^*$$

$$= \sum_{s'} \tau_0 \tau_N \begin{pmatrix} \kappa \\ k \end{pmatrix}^* \begin{pmatrix} \mu \\ m \end{pmatrix}^* \begin{pmatrix} \nu \\ n \end{pmatrix}^* [O^{\kappa *}\ N^{\mu *}]_{n*}^{\nu * s'}\ A_{ss'} \qquad \text{(A2.7)}$$

where τ_0, τ_N are time signatures of the hermitian operators 0,N. Using results of this kind we can show that

$$(R_{\rho\rho'}^{k\ell\ell'})^* = \tau_\Lambda \tau_\kappa\ R_{\rho\rho'}^{k\ell\ell'} \qquad \text{(A2.8)}$$

In the quadratic $\sum_{k\ell\ell'} R_{\rho\rho'}^{k\ell\ell'}\ (R_{\sigma\sigma'}^{k\ell\ell'})^*$ these phases will cancel and so the expression is real and we have that $I(\underline{e}\ \underline{e}') = I(\underline{\tilde{e}}\ \underline{\tilde{e}}')$ for the vibrational Raman effect. To produce a minus sign in this expression one needs to form a quadratic for which the phases of equation (A2.8) do not cancel. This will require a time reversal odd interaction in one of the amplitude terms.

TABLES

The phase choices adopted for these tables are those of Butler (1981). In evaluating table 2 we used the $SO_3 \supset SO_2$ 3JM symbols of Rotenberg et al (1959) and Butler's transformation coefficients (see also Reid (1981)). Tables 4-10 were generated on a Burroughs 6700 series computer using exact arithmetic routines. This produced results directly in surd form. The only exceptions were for the large matrices (> 12 x 12) which were inverted numerically and then converted back to surd form.

Table 1: Notation for Labelling Point Group Irreps

We list the notations of Butler (1981), Koster et al. (1963) and also Mulliken. We use Butler's notation throughout. In this notation $0 \equiv$ identity, $-\lambda \equiv \lambda^*$, $\tilde{\lambda} = \lambda \otimes \tilde{0}$, $\frac{1}{2} \sim |j = m = \frac{1}{2}\rangle$ etc. For groups containing the inversion i.e. C_{nh}, D_{nh}, $(n \neq 3)$ C_{3i}, D_{3d}, T_h, O_h, we have in the three notations that $\lambda \to \lambda^{\pm}$, $\Gamma \to \Gamma^{\pm}$, $X \to X_{g/u}$ for irreps even/odd under inversion.

C_2, C_{2h}, C_s
$(2, 2/m, m)$

	0	$\frac{1}{2}$	$-\frac{1}{2}$	1
	Γ_1	Γ_3	Γ_4	Γ_2
C_2:	A			B
C_s:	A′			A″

C_3, C_{3i}
$(3, \bar{3})$

0	$\frac{1}{2}$	$-\frac{1}{2}$	1	-1	$\frac{3}{2}$
Γ_1	Γ_4	Γ_5	Γ_2	Γ_3	Γ_6
A			E		

C_4, C_{4h}, S_4
$(4, 4/m, \bar{4})$

0	$\frac{1}{2}$	$-\frac{1}{2}$	1	-1	$\frac{3}{2}$	$-\frac{3}{2}$	2
Γ_1	Γ_5	Γ_6	Γ_3	Γ_4	Γ_8	Γ_7	Γ_2
A			E				B

C_6, C_{3h}, C_{6h}
$(6, \bar{6}, 6/m)$

	0	$\frac{1}{2}$	$-\frac{1}{2}$	1	-1	$\frac{5}{2}$	$-\frac{5}{2}$	2	-2	$\frac{3}{2}$	$-\frac{3}{2}$	3
	Γ_1	Γ_7	Γ_8	Γ_5	Γ_6	Γ_{12}	Γ_{11}	Γ_3	Γ_2	Γ_{10}	Γ_9	Γ_4
C_6:	A			E_1				E_2				B
C_{3h}:	A′			E″				E′				A″

D_2, C_{2v}, D_{2h}
(222, mm2, mmm)

	0	$\frac{1}{2}$	$\tilde{0}$	1	$\tilde{1}$
	Γ_1	Γ_5	Γ_3	Γ_2	Γ_4
D_2:	A_1	E′	B_1	B_2	B_3
C_{2v}:	A_1		A_2	B_1	B_2

D_3, C_{3v}, D_{3d},
(32, 3m, $\bar{3}$m

0	$\frac{1}{2}$	$\tilde{0}$	1	$\frac{1}{2}$	$-\frac{1}{2}$
Γ_1	Γ_4	Γ_2	Γ_3	Γ_5	Γ_6
A_1	E′	A_2	E	E″	

D_4, D_{4h}, C_{4v}, D_{2d}
(422, 4/mmm, 4mm, $\bar{4}$2m)

0	$\frac{1}{2}$	$\tilde{0}$	1	$\frac{1}{2}$	2	$\tilde{2}$
Γ_1	Γ_6	Γ_2	Γ_5	Γ_7	Γ_3	Γ_4
A_1	E′	A_2	E	E″	B_1	B_2

D_6, C_{6v}, D_{3h}, D_{6h}
(622, 6mm, $\bar{6}$m2, 6/mmm)

	0	$\frac{1}{2}$	$\tilde{0}$	1	$\frac{1}{2}$	2	$\frac{1}{2}$	3	$\tilde{3}$
	Γ_1	Γ_7	Γ_2	Γ_5	Γ_9	Γ_6	Γ_8	Γ_3	Γ_4
D_6:	A_1	E′	A_2	E_1	E‴	E_2	E″	B_1	B_2
D_{3h}:	A_1'		A_2'	E″		E′		A_1''	A_2''
C_{6v}:	A_1		A_2	E_1		E_2		B_2	B_1

T, T_h
(23, m3)

0	$\frac{1}{2}$	1	$\frac{1}{2}$	$-\frac{1}{2}$	2	-2
Γ_1	Γ_5	Γ_4	Γ_6	Γ_7	Γ_2	Γ_3
A_1	E′	T	E″	E‴	E	

O, O_h, T_d
(432, m3m, $\bar{4}$3m)

0	$\frac{1}{2}$	1	$\frac{1}{2}$	2	$\tilde{1}$	$\frac{\tilde{1}}{2}$	$\tilde{0}$
Γ_1	Γ_6	Γ_4	Γ_8	Γ_3	Γ_5	Γ_7	Γ_2
A_1	E′	T_1	U′	E	T_2	E″	A_2

K

0	$\frac{1}{2}$	1	$\frac{1}{2}$	2	$\frac{1}{2}$	3	$\tilde{1}$	$\frac{\tilde{1}}{2}$
A_1	E′	T_1	U′	V	W′	U	T_2	E″

Table 2: Coupling Coefficients $\langle 1\rho, 1\rho' | J\lambda\mu\nu\rangle$

We list the coupling coefficients (equation 2.33) in several group-subgroup schemes. The columns are labelled $|J\lambda\mu\nu\rangle$ - the additional subscript for $K \to D_3$ distinguishing the two branchings $2(K) \to 1(D_3)$. We indicate the chain which we have used for each group G by the multiplicity label r = 0,1, ... beneath the irrep labels. An asterisk on r indicates that $\epsilon_r^\mu = -1$, otherwise $\epsilon_r^\mu = +1$. We also list the transformation coefficients $\langle 1^- \rho | 1^- \lambda\mu\nu\rangle$ beneath each table.

The chiral groups (C_n, D_n, T,O,K) have the same transformation properties when branching from J^+, J^-. For groups containing the inversion (C_{nh}, D_{nh} $(n \neq 3)$, C_{3i}, D_{3d}, T_h, O_h) we can use the same tables but read $\lambda^+(\lambda^-)$ when branching from $J^+(J^-)$. Groups containing a reflection transform in the following way when branching from J^+ ($C_s \sim C_2$, $C_{2v} \sim D_2$, $C_{3h} \sim C_6$, $C_{3v} \sim D_3$, $S_4 \sim C_4$, $C_{4v} \sim D_4$, $C_{6v} \sim D_6$, $D_{2d} \sim D_4$, $D_{3h} \sim D_6$, $T_d \sim O$) but have different properties when branching from J^-. We include tables for this case. For $\rho \neq \rho'$, $\rho\rho' = +(-)\ \rho'\rho$ for J even(odd).

SO_3-K-D_3-C_3

	$\lvert 0000\rangle$ 000	$\lvert 11\tilde{0}0\rangle$ 002*	$\lvert 111\ 1\rangle$ 02 2	$\lvert 111\text{-}1\rangle$ 02 2	$\lvert 2200\rangle$ 011	$\lvert 22_1 11\rangle$ 0 00	$\lvert 22_0 11\rangle$ 0 11	$\lvert 22_1 1\text{-}1\rangle$ 0 0 0	$\lvert 22_0 1\text{-}1\rangle$ 0 1 1
xx	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{-1}{\sqrt{6}}$	$\frac{-1}{2}$	-	$\frac{-1}{2}$	-
yy	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{-1}{\sqrt{6}}$	$\frac{1}{2}$	-	$\frac{1}{2}$	-
zz	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{\sqrt{2}}{\sqrt{3}}$	-	-	-	-
xy	-	$\frac{i}{\sqrt{2}}$	-	-	-	$\frac{-i}{2}$	-	$\frac{i}{2}$	-
yz	-	-	$\frac{i}{2}$	$\frac{-i}{2}$	-	-	$\frac{i}{2}$	-	$\frac{-i}{2}$
zx	-	-	$\frac{1}{2}$	$\frac{1}{2}$	-	-	$\frac{-1}{2}$	-	$\frac{-1}{2}$

x	-	$\frac{-i}{\sqrt{2}}$	$\frac{i}{\sqrt{2}}$	
y	-	$\frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	
z	-i	-	-	

SO_3-D_∞-D_6-C_6

	$\lvert 0000\rangle$ 00	$\lvert \tilde{1}000\rangle$ 02*	$\lvert 1111\rangle$ 11	$\lvert 111\text{-}1\rangle$ 1 1	$\lvert 2000\rangle$ 11	$\lvert 2222\rangle$ 00	$\lvert 222\text{-}2\rangle$ 0 0	$\lvert 2111\rangle$ 00	$\lvert 211\text{-}1\rangle$ 0 0
xx	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{1}{\sqrt{6}}$	$\frac{1}{2}$	$\frac{1}{2}$	-	-
yy	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{1}{\sqrt{6}}$	$\frac{-1}{2}$	$\frac{-1}{2}$	-	-
zz	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{-\sqrt{2}}{\sqrt{3}}$	-	-	-	-
xy	-	$\frac{i}{\sqrt{2}}$	-	-	-	$\frac{-i}{2}$	$\frac{i}{2}$	-	-
yz	-	-	$\frac{i}{2}$	$\frac{-i}{2}$	-	-	-	$\frac{-i}{2}$	$\frac{i}{2}$
zx	-	-	$\frac{1}{2}$	$\frac{1}{2}$	-	-	-	$\frac{1}{2}$	$\frac{1}{2}$

x	-	$\frac{-i}{\sqrt{2}}$	$\frac{i}{\sqrt{2}}$
y	-	$\frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$
z	-i	-	-

SO_3-O-D_4-C_4

	$\lvert 0000\rangle$ 000	$\lvert 1\tilde{1}00\rangle$ 002*	$\lvert 1111\rangle$ 011	$\lvert 111\text{-}1\rangle$ 01 1	$\lvert 2200\rangle$ 011	$\lvert 2222\rangle$ 000	$\lvert \tilde{2}\tilde{1}22\rangle$ 00 1*	$\lvert \tilde{2}\tilde{1}11\rangle$ 000	$\lvert \tilde{2}\tilde{1}1\text{-}1\rangle$ 00 0
xx	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{-1}{\sqrt{6}}$	$\frac{1}{\sqrt{2}}$	-	-	-
yy	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{-1}{\sqrt{6}}$	$\frac{-1}{\sqrt{2}}$	-	-	-
zz	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{\sqrt{2}}{\sqrt{3}}$	-	-	-	-
xy	-	$\frac{i}{\sqrt{2}}$	-	-	-	-	$\frac{i}{\sqrt{2}}$	-	-
yz	-	-	$\frac{i}{2}$	$\frac{-i}{2}$	-	-	-	$\frac{i}{2}$	$\frac{-i}{2}$
zx	-	-	$\frac{1}{2}$	$\frac{1}{2}$	-	-	-	$\frac{-1}{2}$	$\frac{-1}{2}$

x	-	$\frac{-i}{\sqrt{2}}$	$\frac{i}{\sqrt{2}}$	
y	-	$\frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	
z	-i	-	-	

SO_3-O-D_4-D_2-C_2

	$\lvert 00000\rangle$ 00	$\lvert 11\tilde{0}\tilde{0}0\rangle$ 14*	$\lvert 11111\rangle$ 12	$\lvert 1111\tilde{1}1\rangle$ 13*	$\lvert 22000\rangle$ 11	$\lvert 22200\rangle$ 23	$\lvert 2\tilde{1}\tilde{2}0\tilde{0}\rangle$ 02*	$\lvert 2\tilde{1}1111\rangle$ 00	$\lvert 2\tilde{1}1\tilde{1}11\rangle$ 01*
xx	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{-1}{\sqrt{6}}$	$\frac{-1}{\sqrt{2}}$	-	-	-
yy	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{-1}{\sqrt{6}}$	$\frac{1}{\sqrt{2}}$	-	-	-
zz	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{\sqrt{2}}{\sqrt{3}}$	-	-	-	-
xy	-	$\frac{i}{\sqrt{2}}$	-	-	-	-	$\frac{i}{\sqrt{2}}$	-	-
yz	-	-		$\frac{-i}{\sqrt{2}}$	-	-	-		$\frac{-i}{\sqrt{2}}$
zx	-	-	$\frac{1}{\sqrt{2}}$	-	-	-	-	$\frac{-1}{\sqrt{2}}$	-

x	-	-	i	
y	-	-1	-	
z	-i	-	-	

SO_3-O-T-D_2-C_2

	$\lvert 00000\rangle$ 0	$\lvert 11\tilde{1}\tilde{0}0\rangle$ 1	$\lvert 1111\rangle$ 1	$\lvert 111\tilde{1}\tilde{1}\rangle$ 1	$\lvert 22200\rangle$ 0	$\lvert 22-200\rangle$ 0	$\lvert 2\tilde{1}1\tilde{0}0\rangle$ ŏ*	$\lvert \tilde{2}1111\rangle$ ŏ*	$\lvert \tilde{2}11\tilde{1}1\rangle$ ŏ*
xx	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{-1}{\sqrt{12}}+\frac{i}{2}$	$\frac{-1}{\sqrt{12}}-\frac{i}{2}$	-	-	-
yy	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{-1}{\sqrt{12}}-\frac{i}{2}$	$\frac{-1}{\sqrt{12}}+\frac{i}{2}$	-	-	-
zz	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	-	-
xy	-	$\frac{i}{\sqrt{2}}$	-	-	-	-	$\frac{-1}{\sqrt{2}}$	-	-
yz	-	-	-	$\frac{-i}{\sqrt{2}}$	-	-	-	-	$\frac{1}{\sqrt{2}}$
zx	-	-	$\frac{1}{\sqrt{2}}$	-	-	-	-	$\frac{i}{\sqrt{2}}$	

x	-	-	i	
y	-	-1	-	
z	-i	-	-	

O_3-O_h-D_{4h}-C_{4v}-C_4

	$\lvert 0^-0^-\tilde{0}0^-\rangle$ 1*	$\lvert 1^-1^-\tilde{0}^-0^-\rangle$ 1*	$\lvert 1^-1^-1^-11\rangle$ 1*	$\lvert 1^-1^-1^-1\text{-}1\rangle$ 1*	$\lvert 2^-2^-0^-\tilde{0}0\rangle$ 2*	$\lvert 2^-2^-2^-\tilde{2}\text{-}2\rangle$ 1*	$\lvert 2^-\tilde{1}^-1^-11\rangle$ 0*	$\lvert 2^-\tilde{1}^-1^-1\text{-}1\rangle$ 0*	$\lvert 2^-\tilde{1}^-\tilde{2}^-22\rangle$ 1*
XX	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{-1}{\sqrt{6}}$	$\frac{1}{\sqrt{2}}$	-	-	-
XY	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{-1}{\sqrt{6}}$	$\frac{-1}{\sqrt{2}}$	-	-	-
ZZ	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{2}{\sqrt{6}}$	-	-	-	-
XY	-	$\frac{-i}{\sqrt{2}}$	-	-	-	-	-	-	$\frac{i}{\sqrt{2}}$
YZ	-	-	$\frac{-i}{\sqrt{2}}$	$\frac{-i}{\sqrt{2}}$	-	-	$\frac{-i}{2}$	$\frac{-i}{2}$	-
ZX	-	-	$\frac{-1}{2}$	$\frac{1}{2}$	-	-	$\frac{1}{2}$	$\frac{-1}{2}$	-

X	-	$\frac{i}{\sqrt{2}}$	$\frac{i}{\sqrt{2}}$	
Y	-	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	
Z	i	-	-	

$O_3 \supset D_{\infty h} \supset D_{6h} \supset C_{6v} \supset C_{3v} \supset C_3$

	$\lvert 0^-0^-0^-\tilde{0}\tilde{0}0^- \rangle$ 1*1*	$\lvert 1^-\tilde{0}^-\tilde{0}^-000^- \rangle$ 1*1*	$\lvert 1^-1^-1^-111^- \rangle$ 1*2*	$\lvert 1^-1^-1^-11\text{-}1^- \rangle$ 1*2*	$\lvert 2^-0^-0^-\tilde{0}\tilde{0}0^- \rangle$ 2*2*	$\lvert 2^-1^-1^-111^- \rangle$ 0*1*	$\lvert 2^-1^-1^-11\text{-}1^- \rangle$ 0*1*	$\lvert 2^-2^-2^-211^- \rangle$ 1*0	$\lvert 2^-2^-2^-21\text{-}1^- \rangle$ 1*0
xx	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{1}{\sqrt{6}}$	-	-	$\frac{-i}{2}$	$\frac{i}{2}$
yy	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{1}{\sqrt{6}}$	-	-	$\frac{i}{2}$	$\frac{-i}{2}$
zz	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{-2}{\sqrt{6}}$	-	-	-	-
xy	-	$\frac{-i}{\sqrt{2}}$	-	-	-	-	-	$\frac{1}{2}$	$\frac{1}{2}$
yz	-	-	$\frac{-i}{2}$	$\frac{-i}{2}$	-	$\frac{i}{2}$	$\frac{i}{2}$	-	-
zx	-	-	$\frac{-1}{2}$	$\frac{1}{2}$	-	$\frac{-1}{2}$	$\frac{1}{2}$	-	-
x		-	$\frac{i}{\sqrt{2}}$	$\frac{i}{\sqrt{2}}$					
y		-	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$					
z		i	-	-					

$O_3 \supset D_{\infty h} \supset D_{6h} \supset D_{3h} \supset C_{3h}$

	$\lvert 0^-0^-0^-33 \rangle$ 10	$\lvert 1^-\tilde{0}^-\tilde{0}^-33 \rangle$ 12*	$\lvert 1^-1^-1^-2\text{-}2 \rangle$ 1 1	$\lvert 1^-1^-1^-22 \rangle$ 11	$\lvert 2^-0^-0^-33 \rangle$ 21	$\lvert 2^-1^-1^-2\text{-}2 \rangle$ 0 0	$\lvert 2^-1^-1^-22 \rangle$ 00	$\lvert 2^-2^-2^-1\text{-}1 \rangle$ 1 1	$\lvert 2^-2^-2^-11 \rangle$ 11
XX	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{1}{\sqrt{6}}$	-	-	$\frac{-1}{2}$	$\frac{-1}{2}$
YY	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{1}{\sqrt{6}}$	-	-	$\frac{1}{2}$	$\frac{1}{2}$
ZZ	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{-2}{\sqrt{6}}$	-	-	-	-
XY	-	$\frac{-i}{\sqrt{2}}$	-	-	-	-	-	$\frac{i}{2}$	$\frac{-i}{2}$
YZ	-	-	$\frac{-i}{2}$	$\frac{i}{2}$	-	$\frac{i}{2}$	$\frac{-i}{2}$	-	-
ZX	-	-	$\frac{-1}{2}$	$\frac{-1}{2}$	-	$\frac{-1}{2}$	$\frac{-1}{2}$	-	-
X		-	$\frac{i}{\sqrt{2}}$	$\frac{-i}{\sqrt{2}}$					
Y		-	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$					
Z		i	-	-					

$O_3 - O_h - D_{4h} - C_{4v} - C_{2v} - C_2$

	$\lvert 0^-0^-0^-\tilde{0}\tilde{0}0\rangle$ 1*	$\lvert 1^-1^-\tilde{0}^-000\rangle$ 1*	$\lvert 1^-1^-1^-1\tilde{1}1\rangle$ 1*	$\lvert 1^-1^-1^-111\rangle$ 1*	$\lvert 2^-2^-0^-\tilde{0}\tilde{0}0\rangle$ 2*	$\lvert 2^-2^-2^-\tilde{2}\tilde{0}0\rangle$ 3*	$\lvert 2^-\tilde{1}^-1^-1\tilde{1}1\rangle$ 0*	$\lvert 2^-\tilde{1}^-1^-111\rangle$ 0*	$\lvert 2^-1^-2^-200\rangle$ 0*
XX	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{-1}{\sqrt{6}}$	$\frac{1}{\sqrt{2}}$	-	-	-
YY	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{-1}{\sqrt{6}}$	$\frac{-1}{\sqrt{2}}$	-	-	-
ZZ	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{2}{\sqrt{6}}$	-	-	-	-
XY	-	$\frac{-i}{\sqrt{2}}$	-	-	-	-	-	-	$\frac{-i}{\sqrt{2}}$
YZ	-	-	-	$\frac{-i}{\sqrt{2}}$	-	-	-	$\frac{-i}{\sqrt{2}}$	-
ZX	-	-	$\frac{1}{\sqrt{2}}$	-	-	-	$\frac{-1}{\sqrt{2}}$	-	-
X		-	-	i					
Y		-	-1	-					
Z		i	-	-					

$O_3 - O_h - D_{4h} - C_{4v} - C_{2v} - C_s$

	$\lvert 0^-0^-0^-\tilde{0}\tilde{0}1\rangle$ 0	$\lvert 1^-1^-\tilde{0}^-000\rangle$ 2	$\lvert 1^-1^-1^-1\tilde{1}1\rangle$ 4*	$\lvert 1^-1^-1^-110\rangle$ 3*	$\lvert 2^-2^-0^-\tilde{0}\tilde{0}1\rangle$ 1	$\lvert 2^-2^-2^-\tilde{2}\tilde{0}1\rangle$ 3	$\lvert 2^-\tilde{1}^-1^-1\tilde{1}1\rangle$ 2*	$\lvert 2^-\tilde{1}^-1^-110\rangle$ 1*	$\lvert 2^-\tilde{1}^-\tilde{2}^-200\rangle$ 0
XX	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{-1}{\sqrt{6}}$	$\frac{1}{\sqrt{2}}$	-	-	-
YY	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{2}{\sqrt{6}}$	-	-	-	-
ZZ	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{-1}{\sqrt{6}}$	$\frac{-1}{\sqrt{2}}$	-	-	-
XY	-	-	$\frac{-i}{\sqrt{2}}$	-	-	-	$\frac{-i}{\sqrt{2}}$	-	-
YZ	-	-	-	$\frac{-i}{\sqrt{2}}$	-	-	-	$\frac{i}{\sqrt{2}}$	-
ZX	-	$\frac{1}{\sqrt{2}}$	-	-	-	-	-	-	$\frac{-1}{\sqrt{2}}$
X		-	-	i					
Y		-1	-	-					
Z		-	i	-					

O_3-O_h-T_d-D_{2d}-S_4

	$\|0\ 0\ \tilde{0}\ 22\rangle$ 110	$\|1\ 1\ \tilde{1}\ \tilde{2}2\rangle$ 112*	$\|1\ 1\ \tilde{1}\ 1\text{-}1\rangle$ 11 1	$\|1\ 1\ \tilde{1}\ 11\rangle$ 111	$\|2\ 2\ 222\rangle$ 121	$\|2\ 2\ 200\rangle$ 110	$\|2\ \tilde{1}\ 11\ 1\rangle$ 10 0	$\|2\ \tilde{1}\ 111\rangle$ 100	$\|2\ \tilde{1}\ 1\tilde{0}0\rangle$ 111*
XX	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{-1}{\sqrt{6}}$	$\frac{-1}{\sqrt{2}}$	-	-	-
YY	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{-1}{\sqrt{6}}$	$\frac{1}{\sqrt{2}}$	-	-	-
ZZ	$\frac{1}{\sqrt{3}}$	-	-	-	$\frac{2}{\sqrt{6}}$	-	-	-	-
XY	-	$\frac{i}{\sqrt{2}}$	-	-	-	-	-	-	$\frac{i}{\sqrt{2}}$
YZ	-	-	$\frac{-i}{2}$	$\frac{i}{2}$	-	-	$\frac{-i}{2}$	$\frac{i}{2}$	-
ZX	-	-	$\frac{-1}{2}$	$\frac{-1}{2}$	-	-	$\frac{1}{2}$	$\frac{1}{2}$	-
X		-	$\frac{i}{\sqrt{2}}$	$\frac{-i}{\sqrt{2}}$					
Y		-	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$					
Z		-i	-	-					

Table 3: Non vanishing terms $c^{\eta\varepsilon}_{j_1 j_2 JM}$

The physical constants contributing to the intensity are given for the standard coupling in the spherical basis. Similar terms for the alternative coupling may be obtained by exchanging η and ε. We list the numbers of terms which will contribute for three situations: for a general scatterer $N = \sum_{\eta\varepsilon} N^{\eta\varepsilon}$, for a real scatterer $N^+ = \sum_{\varepsilon} N^{+\varepsilon}$, and for a real symmetric scatterer N^{++}. The label $\theta = c$ represents the linear combination

$$|4c\rangle = \sqrt{\frac{5}{12}}\,|44+\rangle + \sqrt{\frac{7}{12}}\,|40\rangle \quad .$$

C_1 symmetry :

($N = 81$, $N^+ = 45$, $N^{++} = 27$)

η	ε	j_1	j_2	j	$m\theta$
+	+	0	0	0	0
+	+	1	1	0	0
+	+	2	2	0	0
+	+	1	1	2	$(0,1\pm,2\pm)$
$\pm$	+	2	0	2	$(0,1\pm,2\pm)$
+	+	2	2	2	$(0,1\pm,2\pm)$
+	+	2	2	4	$(0,1\pm,2\pm,3\pm,4\pm)$
$\pm$	-	1	0	1	$(0,1\pm)$
$\pm$	-	2	1	1	$(0,1\pm)$
$\pm$	-	2	1	2	$(0,1\pm,2\pm)$
$\pm$	-	2	1	3	$(0,1\pm,2\pm,3\pm)$
-	+	1	1	1	$(0,1\pm)$
-	+	2	2	1	$(0,1\pm)$
-	+	2	2	3	$(0,1\pm,2\pm,3\pm)$

C_2, C_s, C_{2h}

($N = 41$, $N^+ = 25$, $N^{++} = 17$)

As for C_1, with the restriction $m = 0 \bmod 2$.

C_3, C_{3i}

($N = 27$, $N^+ = 15$, $N^{++} = 9$)

As for C_1, with the restriction $m = 0 \bmod 3$.

C_4, C_{4i}

($N = 21$, $N^+ = 13$, $N^{++} = 9$)

As for C_1, with the restriction $m = 0 \bmod 4$.

C_6, C_{6h}, C_{3h}

($N = 19$, $N^+ = 11$, $N^{++} = 7$)

As for C_1, with the restriction $m = 0$.

D_2, D_{2h}, C_{2v}

(N = 21, N^+ = 15, N^{++}= 12)

η	ε	j_1	j_2	j	mθ
+	+	0	0	0	0
+	+	1	1	0	0
+	+	2	2	0	0
+	+	1	1	2	(0,2+)
±	+	2	0	2	(0,2+)
+	+	2	2	2	(0,2+)
+	+	2	2	4	(0,2+,4+)
±	-	2	1	2	(0,2+)
±	-	2	1	3	2 -
-	+	2	2	3	2 -

D_3, C_{3v}, D_{3d}

(N = 14, N^+ = 10, N^{++}= 8)

η	ε	j_1	j_2	j	mθ
+	+	0	0	0	0
+	+	1	1	0	0
+	+	2	2	0	0
+	+	1	1	2	0
±	+	2	0	2	0
+	+	2	2	2	0
+	+	2	2	4	(0,3-)
±	-	2	1	2	0
±	-	2	1	3	3+
-	+	2	2	3	3+

D_4, D_{2d}, D_{4h}, C_{4v}

(N = 11, N^+ = 9, N^{++}= 8)

As for D_2, with the restriction m = 0 mod 4.

D_6, D_{3h}, D_{6h}, C_{6v}

(N = 10, N^+ = 8, N^{++}= 7)

As for D_2, with the restriction m = 0.

O, O_h, T_d

(N = N^+ = N^{++}= 4)

η	ε	j_1	j_2	j	mθ
+	+	0	0	0	0
+	+	1	1	0	0
+	+	2	2	0	0
+	+	2	2	4	c

T, T_h

(N = 7, N^+ = 5, N^{++}= 4)

η	ε	j_1	j_2	j	mθ
+	+	0	0	0	0
+	+	1	1	0	0
+	+	2	2	0	0
+	+	2	2	4	c
±	-	2	1	3	2 -
-	+	2	2	3	2 -

R_3, K

(N = N^+ = N^{++}= 3)

η	ε	j_1	j_2	j	mθ
+	+	0	0	0	0
+	+	1	1	0	0
+	+	2	2	0	0

Table 4: Cartesian Basis → Experimental Spectra. $F^{++}_{\rho\rho',\sigma\sigma'}(\underline{e}\ \underline{e}')$

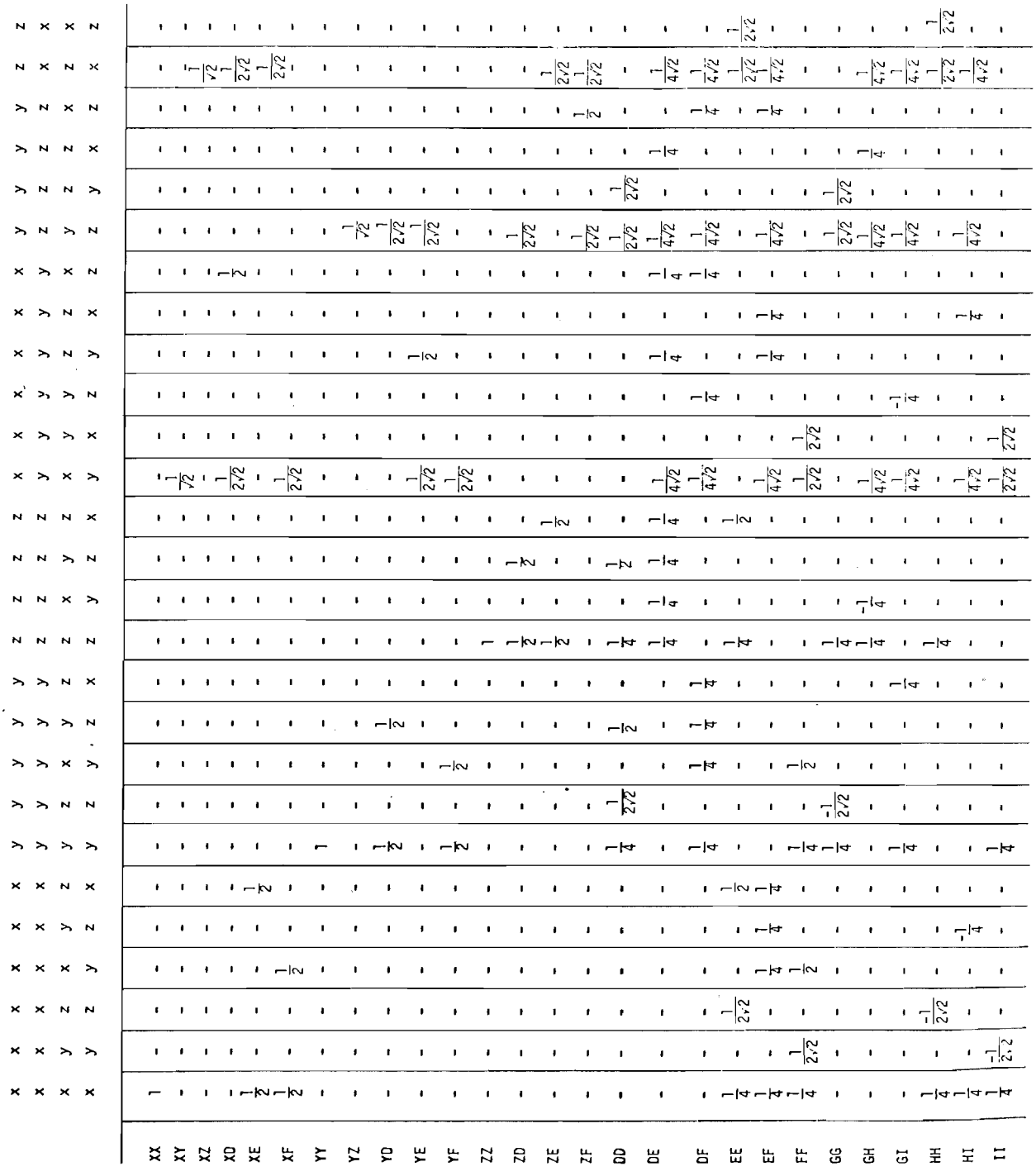


Table 5: Cartesian Basis ↔ Spherical Basis $T^{j_1 j_2 JM\theta}_{\rho\rho'\sigma\sigma'++}$

	j_1	0	0	0	0	0	0	1	1	1	1	1	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
	j_2	0	2	2	2	2	2	1	1	1	1	1	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
	J	0	2	2	2	2	2	0	2	2	2	2	2	0	2	2	2	2	2	4	4	4	4	4	4	4	4	4	4
	$m\theta$	0	0	1+	1-	2+	2-	0	0	1+	1-	2+	2-	0	0	1+	1-	2+	2-	0	1+	1-	2+	2-	3+	3-	4+	4-	c
X X X X		$\frac{1}{3}$	$\frac{1}{3}$	-	-	$\frac{-1}{\sqrt{3}}$	-	-	-	-	-	-	-	$\frac{2}{3\sqrt{5}}$	$\frac{2}{3\sqrt{14}}$	-	-	$\frac{-2}{\sqrt{42}}$	-	$\frac{3}{2\sqrt{70}}$	-	-	$\frac{-1}{\sqrt{14}}$	-	-	-	$\frac{1}{2\sqrt{2}}$	-	$\frac{2}{\sqrt{30}}$
X X Y Y		$\frac{\sqrt{2}}{3}$	$\frac{\sqrt{2}}{3}$	-	-	-	-	-	-	-	-	-	-	$\frac{-2}{3\sqrt{10}}$	$\frac{-4}{3\sqrt{7}}$	-	-	-	-	$\frac{1}{2\sqrt{35}}$	-	-	-	-	-	-	$\frac{-1}{2}$	-	$\frac{-1}{\sqrt{15}}$
X X Z Z		$\frac{\sqrt{2}}{3}$	$\frac{-\sqrt{2}}{6}$	-	-	$\frac{-1}{\sqrt{6}}$	-	-	-	-	-	-	-	$\frac{-2}{3\sqrt{10}}$	$\frac{2}{3\sqrt{7}}$	-	-	$\frac{2}{\sqrt{21}}$	-	$\frac{-2}{\sqrt{35}}$	-	-	$\frac{1}{\sqrt{7}}$	-	-	-	-	-	$\frac{-1}{\sqrt{15}}$
X X X Y		-	-	-	-	-	$\frac{1}{\sqrt{3}}$	-	-	-	-	-	-	-	-	-	-	-	$\frac{2}{\sqrt{42}}$	-	-	-	-	$\frac{1}{\sqrt{14}}$	-	-	-	$\frac{-1}{\sqrt{2}}$	-
X X Y Z		-	-	-	$\frac{1}{\sqrt{3}}$	-	-	-	-	-	-	-	-	-	-	-	$\frac{-4}{\sqrt{42}}$	-	-	-	-	$\frac{1}{\sqrt{28}}$	-	-	-	$\frac{-1}{2}$	-	-	-
X X Z X		-	-	$\frac{-1}{\sqrt{3}}$	-	-	-	-	-	-	-	-	-	-	-	$\frac{-2}{\sqrt{42}}$	-	-	-	-	$\frac{-3}{\sqrt{28}}$	-	-	-	$\frac{1}{2}$	-	-	-	-
Y Y Y Y		$\frac{1}{3}$	$\frac{1}{3}$	-	-	$\frac{1}{\sqrt{3}}$	-	-	-	-	-	-	-	$\frac{2}{3\sqrt{5}}$	$\frac{2}{3\sqrt{14}}$	-	-	$\frac{2}{\sqrt{42}}$	-	$\frac{3}{2\sqrt{70}}$	-	-	$\frac{1}{\sqrt{14}}$	-	-	-	$\frac{1}{2\sqrt{2}}$	-	$\frac{2}{\sqrt{30}}$
Y Y Z Z		$\frac{\sqrt{2}}{3}$	$\frac{\sqrt{2}}{6}$	-	-	$\frac{1}{\sqrt{6}}$	-	-	-	-	-	-	-	$\frac{-2}{3\sqrt{10}}$	$\frac{2}{3\sqrt{7}}$	-	-	$\frac{-2}{\sqrt{21}}$	-	$\frac{-2}{\sqrt{35}}$	-	-	$\frac{-1}{\sqrt{7}}$	-	-	-	-	-	$\frac{-1}{\sqrt{15}}$
Y Y X Y		-	-	-	-	-	$\frac{1}{\sqrt{3}}$	-	-	-	-	-	-	-	-	-	-	-	$\frac{2}{\sqrt{42}}$	-	-	-	-	$\frac{1}{\sqrt{14}}$	-	-	-	$\frac{1}{\sqrt{2}}$	-
Y Y Y Z		-	-	-	$\frac{1}{\sqrt{3}}$	-	-	-	-	-	-	-	-	-	-	$\frac{2}{\sqrt{42}}$	-	-	-	-	-	$\frac{3}{\sqrt{28}}$	-	-	-	$\frac{1}{2}$	-	-	-
Y Y Z X		-	-	$\frac{-1}{\sqrt{3}}$	-	-	-	-	-	-	-	-	-	-	-	$\frac{4}{\sqrt{42}}$	-	-	-	-	$\frac{-1}{\sqrt{28}}$	-	-	-	$\frac{-1}{2}$	-	-	-	-
Z Z Z Z		$\frac{1}{3}$	$\frac{-2}{3}$	-	-	-	-	-	-	-	-	-	-	$\frac{2}{3\sqrt{5}}$	$\frac{-4}{3\sqrt{14}}$	-	-	-	-	$\frac{4}{\sqrt{70}}$	-	-	-	-	-	-	-	-	$\frac{2}{\sqrt{30}}$
Z Z X Y		-	-	-	-	-	$\frac{1}{\sqrt{3}}$	-	-	-	-	-	-	-	-	-	-	-	$\frac{-4}{\sqrt{42}}$	-	-	-	-	$\frac{-2}{\sqrt{14}}$	-	-	-	-	-
Z Z Y Z		-	-	-	$\frac{1}{\sqrt{3}}$	-	-	-	-	-	-	-	-	-	-	-	$\frac{2}{\sqrt{42}}$	-	-	-	-	$\frac{-2}{\sqrt{7}}$	-	-	-	-	-	-	-	-
Z Z Z X		-	-	$\frac{-1}{\sqrt{3}}$	-	-	-	-	-	-	-	-	-	-	-	$\frac{-2}{\sqrt{42}}$	-	-	-	-	$\frac{2}{\sqrt{7}}$	-	-	-	-	-	-	-	-	-
X Y X Y		-	-	-	-	-	-	$\frac{1}{\sqrt{6}}$	$\frac{-1}{\sqrt{3}}$	-	-	-	-	$\frac{1}{\sqrt{10}}$	$\frac{1}{\sqrt{7}}$	-	-	-	-	$\frac{1}{2\sqrt{35}}$	-	-	-	-	-	-	$\frac{-1}{2}$	-	$\frac{-1}{\sqrt{15}}$
X Y Y X		-	-	-	-	-	-	$\frac{-1}{\sqrt{6}}$	$\frac{1}{\sqrt{3}}$	-	-	-	-	$\frac{1}{\sqrt{10}}$	$\frac{1}{\sqrt{7}}$	-	-	-	-	$\frac{1}{2\sqrt{35}}$	-	-	-	-	-	-	$\frac{-1}{2}$	-	$\frac{-1}{\sqrt{15}}$
X Y Y Z		-	-	-	-	-	-	-	-	$\frac{-1}{\sqrt{2}}$	-	-	-	-	-	$\frac{-3}{\sqrt{42}}$	-	-	-	-	$\frac{-1}{\sqrt{28}}$	-	-	-	$\frac{-1}{2}$	-	-	-	-	-
X Y Z Y		-	-	-	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	-	-	-	-	-	$\frac{-3}{\sqrt{42}}$	-	-	-	-	$\frac{-1}{\sqrt{28}}$	-	-	-	$\frac{-1}{2}$	-	-	-	-	-
X Y Z X		-	-	-	-	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	-	-	-	-	$\frac{3}{\sqrt{42}}$	-	-	-	-	-	$\frac{1}{\sqrt{28}}$	-	-	-	$\frac{-1}{2}$	-	-	-	-
X Y X Z		-	-	-	-	-	-	-	-	-	$\frac{-1}{\sqrt{2}}$	-	-	-	-	$\frac{3}{\sqrt{42}}$	-	-	-	-	-	$\frac{1}{\sqrt{28}}$	-	-	-	$\frac{-1}{2}$	-	-	-	-
Y Z Y Z		-	-	-	-	-	-	$\frac{1}{\sqrt{6}}$	$\frac{1}{2\sqrt{3}}$	-	-	$\frac{-1}{2}$	-	$\frac{1}{\sqrt{10}}$	$\frac{-1}{2\sqrt{7}}$	-	-	$\frac{3}{2\sqrt{21}}$	-	$\frac{-2}{\sqrt{35}}$	-	-	$\frac{-1}{\sqrt{7}}$	-	-	-	-	-	-	$\frac{-1}{\sqrt{15}}$
Y Z Z Y		-	-	-	-	-	-	$\frac{-1}{\sqrt{6}}$	$\frac{-1}{2\sqrt{3}}$	-	-	$\frac{1}{2}$	-	$\frac{1}{\sqrt{10}}$	$\frac{-1}{2\sqrt{7}}$	-	-	$\frac{3}{2\sqrt{21}}$	-	$\frac{-2}{\sqrt{35}}$	-	-	$\frac{-1}{\sqrt{7}}$	-	-	-	-	-	-	$\frac{-1}{\sqrt{15}}$
Y Z Z X		-	-	-	-	-	-	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	-	-	-	-	-	$\frac{3}{\sqrt{42}}$	-	-	-	-	$\frac{-2}{\sqrt{14}}$	-	-	-	-	-	-
Y Z X Z		-	-	-	-	-	-	-	-	-	-	-	$\frac{-1}{\sqrt{2}}$	-	-	-	-	-	$\frac{3}{\sqrt{42}}$	-	-	-	-	$\frac{-2}{\sqrt{14}}$	-	-	-	-	-	-
Z X Z X		-	-	-	-	-	-	$\frac{-1}{\sqrt{6}}$	$\frac{1}{2\sqrt{3}}$	-	-	$\frac{1}{2}$	-	$\frac{1}{\sqrt{10}}$	$\frac{-1}{2\sqrt{7}}$	-	-	$\frac{-3}{2\sqrt{21}}$	-	$\frac{-2}{\sqrt{35}}$	-	-	$\frac{1}{\sqrt{7}}$	-	-	-	-	-	-	$\frac{-1}{\sqrt{15}}$
Z X X Z		-	-	-	-	-	-	$\frac{-1}{\sqrt{6}}$	$\frac{-1}{2\sqrt{3}}$	-	-	$\frac{-1}{2}$	-	$\frac{1}{\sqrt{10}}$	$\frac{-1}{2\sqrt{7}}$	-	-	$\frac{-3}{2\sqrt{21}}$	-	$\frac{-2}{\sqrt{35}}$	-	-	$\frac{1}{\sqrt{7}}$	-	-	-	-	-	-	$\frac{-1}{\sqrt{15}}$

Table 6: Experimental Spectra ← Spherical Basis $F^{++}_{j_1 j_2 JM\theta}(\underline{e}\,\underline{e}')$

j_1	0	0	0	0	0	0	1	1	1	1	1	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
j_2	0	2	2	2	2	2	1	1	1	1	1	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
J	0	2	2	2	2	2	0	2	2	2	2	2	0	2	2	2	2	2	4	4	4	4	4	4	4	4	4	4	4
M	0	0	1+	1-	2+	2-	0	0	1+	1-	2+	2-	0	0	1+	1-	2+	2-	0	1+	1-	2+	2-	3+	3-	4+	4-	∞	
XX	$\frac{1}{3}$	$\frac{1}{3}$	-	-	$\frac{-1}{\sqrt{3}}$	-	-	-	-	-	-	-	$\frac{2}{3\sqrt{5}}$	$\frac{2}{3\sqrt{14}}$	-	-	$\frac{-2}{\sqrt{42}}$	-	$\frac{3}{2\sqrt{70}}$	-	-	$\frac{-1}{\sqrt{14}}$	-	-	-	$\frac{1}{2\sqrt{2}}$	-	$\frac{2}{\sqrt{30}}$	
XY	-	-	-	-	-	-	$\frac{1}{2\sqrt{3}}$	$\frac{-1}{\sqrt{6}}$	-	-	-	-	$\frac{1}{2\sqrt{5}}$	$\frac{1}{\sqrt{14}}$	-	-	-	-	$\frac{1}{2\sqrt{70}}$	-	-	-	-	-	-	$\frac{-1}{2\sqrt{2}}$	-	$\frac{-1}{\sqrt{30}}$	
XZ	-	-	-	-	-	-	$\frac{1}{2\sqrt{3}}$	$\frac{1}{2\sqrt{6}}$	-	-	$\frac{1}{2\sqrt{2}}$	-	$\frac{1}{2\sqrt{5}}$	$\frac{-1}{2\sqrt{14}}$	-	-	$\frac{-3}{3\sqrt{42}}$	-	$\frac{-2}{\sqrt{70}}$	-	-	$\frac{1}{\sqrt{14}}$	-	-	-	-	-	$\frac{1}{\sqrt{30}}$	
XO	-	-	-	-	-	-	$\frac{1}{2\sqrt{3}}$	$\frac{-1}{4\sqrt{6}}$	-	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{4\sqrt{2}}$	-	$\frac{1}{2\sqrt{5}}$	$\frac{1}{4\sqrt{14}}$	-	$\frac{3}{2\sqrt{42}}$	$\frac{-3}{4\sqrt{42}}$	-	$\frac{-3}{4\sqrt{70}}$	-	$\frac{1}{2\sqrt{28}}$	$\frac{1}{2\sqrt{14}}$	-	-	$\frac{-1}{4}$	$\frac{-1}{4\sqrt{2}}$	-	$\frac{-1}{\sqrt{30}}$	
XE	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{-1}{2\sqrt{3}}$	-	$\frac{-1}{2\sqrt{3}}$	-	$\frac{1}{4\sqrt{3}}$	$\frac{1}{4\sqrt{6}}$	-	-	$\frac{1}{4\sqrt{2}}$	-	$\frac{7}{12\sqrt{5}}$	$\frac{1}{12\sqrt{14}}$	$\frac{-1}{\sqrt{42}}$	-	$\frac{-7}{4\sqrt{42}}$	-	$\frac{-1}{4\sqrt{70}}$	$\frac{-3}{2\sqrt{28}}$	-	-	-	$\frac{1}{4}$	-	$\frac{1}{4\sqrt{2}}$	-	$\frac{1}{2\sqrt{30}}$	
XF	$\frac{1}{6}$	$\frac{1}{6}$	-	-	$\frac{-1}{2\sqrt{3}}$	$\frac{1}{2\sqrt{3}}$	$\frac{1}{4\sqrt{3}}$	$\frac{-1}{2\sqrt{6}}$	-	-	-	-	$\frac{7}{12\sqrt{5}}$	$\frac{5}{6\sqrt{14}}$	-	-	$\frac{-1}{\sqrt{42}}$	$\frac{1}{\sqrt{42}}$	$\frac{1}{\sqrt{70}}$	-	-	$\frac{-1}{2\sqrt{14}}$	$\frac{1}{2\sqrt{14}}$	-	-	-	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{30}}$	
YY	$\frac{1}{3}$	$\frac{1}{3}$	-	-	$\frac{1}{\sqrt{3}}$	-	-	-	-	-	-	-	$\frac{2}{3\sqrt{5}}$	$\frac{2}{3\sqrt{14}}$	-	-	$\frac{2}{\sqrt{42}}$	-	$\frac{3}{2\sqrt{70}}$	-	-	$\frac{1}{\sqrt{14}}$	-	-	-	$\frac{1}{2\sqrt{2}}$	-	$\frac{2}{\sqrt{30}}$	
YZ	-	-	-	-	-	-	$\frac{1}{2\sqrt{3}}$	$\frac{1}{2\sqrt{6}}$	-	-	$\frac{-1}{2\sqrt{2}}$	-	$\frac{1}{2\sqrt{5}}$	$\frac{-1}{2\sqrt{14}}$	-	-	$\frac{3}{2\sqrt{42}}$	-	$\frac{-2}{\sqrt{70}}$	-	-	$\frac{-1}{\sqrt{14}}$	-	-	-	-	-	$\frac{-1}{\sqrt{30}}$	
YD	$\frac{1}{6}$	$\frac{1}{6}$	-	$\frac{1}{2\sqrt{3}}$	$\frac{1}{2\sqrt{3}}$	-	$\frac{1}{4\sqrt{3}}$	$\frac{1}{4\sqrt{6}}$	-	-	$\frac{-1}{4\sqrt{2}}$	-	$\frac{7}{12\sqrt{5}}$	$\frac{1}{12\sqrt{14}}$	-	$\frac{1}{\sqrt{42}}$	$\frac{7}{4\sqrt{42}}$	-	$\frac{-1}{4\sqrt{70}}$	-	$\frac{3}{2\sqrt{28}}$	-	-	-	$\frac{1}{4}$	$\frac{1}{4\sqrt{2}}$	-	$\frac{1}{2\sqrt{30}}$	
YE	-	-	-	-	-	-	$\frac{1}{2\sqrt{3}}$	$\frac{-1}{4\sqrt{6}}$	$\frac{1}{2\sqrt{2}}$	-	$\frac{-1}{4\sqrt{2}}$	-	$\frac{1}{2\sqrt{5}}$	$\frac{1}{4\sqrt{14}}$	$\frac{-3}{2\sqrt{42}}$	-	$\frac{3}{4\sqrt{42}}$	-	$\frac{-3}{4\sqrt{70}}$	$\frac{-1}{2\sqrt{28}}$	-	$\frac{-1}{2\sqrt{14}}$	-	$\frac{-1}{4}$	-	$\frac{-1}{4\sqrt{2}}$	-	$\frac{-1}{\sqrt{30}}$	
YF	$\frac{1}{6}$	$\frac{1}{6}$	-	-	$\frac{1}{2\sqrt{3}}$	$\frac{1}{2\sqrt{3}}$	$\frac{1}{4\sqrt{3}}$	$\frac{-1}{2\sqrt{6}}$	-	-	-	-	$\frac{7}{12\sqrt{5}}$	$\frac{5}{6\sqrt{14}}$	-	-	$\frac{1}{\sqrt{42}}$	$\frac{1}{\sqrt{42}}$	$\frac{1}{\sqrt{70}}$	-	-	$\frac{1}{2\sqrt{14}}$	$\frac{1}{2\sqrt{14}}$	-	-	-	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{30}}$	
ZZ	$\frac{1}{3}$	$\frac{-2}{3}$	-	-	-	-	-	-	-	-	-	-	$\frac{2}{3\sqrt{5}}$	$\frac{-4}{3\sqrt{14}}$	-	-	-	-	$\frac{4}{\sqrt{70}}$	-	-	-	-	-	-	-	-	$\frac{2}{\sqrt{30}}$	
ZD	$\frac{1}{6}$	$\frac{-1}{3}$	-	$\frac{1}{2\sqrt{3}}$	-	-	$\frac{1}{4\sqrt{3}}$	$\frac{1}{4\sqrt{6}}$	-	-	$\frac{-1}{4\sqrt{2}}$	-	$\frac{7}{12\sqrt{5}}$	$\frac{-11}{12\sqrt{14}}$	-	$\frac{1}{\sqrt{42}}$	$\frac{3}{4\sqrt{42}}$	-	$\frac{1}{\sqrt{70}}$	-	$\frac{-2}{\sqrt{28}}$	$\frac{-1}{2\sqrt{14}}$	-	-	-	-	-	$\frac{1}{2\sqrt{30}}$	
ZE	$\frac{1}{6}$	$\frac{-1}{3}$	$\frac{-1}{2\sqrt{3}}$	-	-	-	$\frac{1}{4\sqrt{3}}$	$\frac{1}{4\sqrt{6}}$	-	-	$\frac{1}{4\sqrt{2}}$	-	$\frac{7}{12\sqrt{5}}$	$\frac{-11}{12\sqrt{14}}$	$\frac{-1}{\sqrt{42}}$	-	$\frac{-3}{4\sqrt{42}}$	-	$\frac{1}{\sqrt{70}}$	$\frac{2}{\sqrt{28}}$	-	$\frac{1}{2\sqrt{14}}$	-	-	-	-	-	$\frac{1}{2\sqrt{30}}$	
ZF	-	-	-	-	-	-	$\frac{1}{2\sqrt{3}}$	$\frac{1}{2\sqrt{6}}$	-	-	-	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{5}}$	$\frac{-1}{2\sqrt{14}}$	-	-	-	$\frac{3}{2\sqrt{42}}$	$\frac{-2}{\sqrt{70}}$	-	-	-	$\frac{-1}{\sqrt{14}}$	-	-	-	-	$\frac{-1}{\sqrt{30}}$	
DD	$\frac{1}{3}$	$\frac{-1}{6}$	-	$\frac{1}{\sqrt{3}}$	$\frac{1}{2\sqrt{3}}$	-	-	-	-	-	-	-	$\frac{2}{3\sqrt{5}}$	$\frac{-1}{3\sqrt{14}}$	-	$\frac{2}{\sqrt{42}}$	$\frac{1}{\sqrt{42}}$	-	$\frac{-13}{8\sqrt{70}}$	-	$\frac{-1}{2\sqrt{28}}$	$\frac{-5}{4\sqrt{14}}$	-	-	$\frac{1}{4}$	$\frac{1}{8\sqrt{2}}$	-	$\frac{-1}{2\sqrt{30}}$	
DE	$\frac{1}{12}$	$\frac{-1}{6}$	$\frac{-1}{4\sqrt{3}}$	$\frac{1}{4\sqrt{3}}$	-	$\frac{1}{4\sqrt{3}}$	$\frac{3}{8\sqrt{3}}$	-	$\frac{-1}{4\sqrt{2}}$	$\frac{1}{4\sqrt{2}}$	-	$\frac{1}{4\sqrt{2}}$	$\frac{13}{24\sqrt{5}}$	$\frac{-1}{3\sqrt{14}}$	$\frac{-5}{4\sqrt{42}}$	$\frac{5}{4\sqrt{42}}$	-	$\frac{-1}{4\sqrt{42}}$	$\frac{1}{8\sqrt{70}}$	$\frac{3}{4\sqrt{28}}$	$\frac{-3}{4\sqrt{28}}$	-	$\frac{-1}{\sqrt{14}}$	$\frac{-1}{8}$	$\frac{-1}{8}$	$\frac{-1}{8\sqrt{2}}$	-	$\frac{-1}{4\sqrt{30}}$	
DF	$\frac{1}{12}$	$\frac{1}{12}$	$\frac{-1}{4\sqrt{3}}$	$\frac{1}{4\sqrt{3}}$	$\frac{1}{4\sqrt{3}}$	$\frac{1}{4\sqrt{3}}$	$\frac{3}{8\sqrt{3}}$	-	$\frac{-1}{4\sqrt{2}}$	$\frac{-1}{4\sqrt{2}}$	-	$\frac{-1}{4\sqrt{2}}$	$\frac{13}{24\sqrt{5}}$	$\frac{1}{6\sqrt{14}}$	$\frac{1}{4\sqrt{42}}$	$\frac{5}{4\sqrt{42}}$	$\frac{-1}{2\sqrt{42}}$	$\frac{5}{4\sqrt{42}}$	$\frac{-1}{2\sqrt{70}}$	$\frac{-1}{2\sqrt{28}}$	$\frac{1}{\sqrt{28}}$	$\frac{1}{4\sqrt{14}}$	$\frac{-1}{4\sqrt{14}}$	$\frac{-1}{4}$	-	-	$\frac{1}{4\sqrt{2}}$	$\frac{-1}{4\sqrt{30}}$	
EE	$\frac{1}{3}$	$\frac{-1}{6}$	$\frac{-1}{\sqrt{3}}$	-	$\frac{-1}{2\sqrt{3}}$	-	-	-	-	-	-	-	$\frac{2}{3\sqrt{5}}$	$\frac{-1}{3\sqrt{14}}$	$\frac{-2}{\sqrt{42}}$	-	$\frac{-1}{\sqrt{42}}$	-	$\frac{-13}{8\sqrt{70}}$	$\frac{1}{2\sqrt{28}}$	-	$\frac{5}{4\sqrt{14}}$	-	$\frac{1}{4}$	-	$\frac{1}{8\sqrt{2}}$	-	$\frac{-1}{2\sqrt{30}}$	
EF	$\frac{1}{12}$	$\frac{1}{12}$	$\frac{-1}{4\sqrt{3}}$	$\frac{1}{4\sqrt{3}}$	$\frac{-1}{4\sqrt{3}}$	$\frac{1}{4\sqrt{3}}$	$\frac{3}{8\sqrt{3}}$	-	$\frac{1}{4\sqrt{2}}$	$\frac{1}{4\sqrt{2}}$	-	$\frac{-1}{4\sqrt{2}}$	$\frac{13}{24\sqrt{5}}$	$\frac{1}{6\sqrt{14}}$	$\frac{-5}{4\sqrt{42}}$	$\frac{-1}{4\sqrt{42}}$	$\frac{-1}{2\sqrt{42}}$	$\frac{5}{4\sqrt{42}}$	$\frac{-1}{2\sqrt{70}}$	$\frac{-1}{2\sqrt{28}}$	$\frac{1}{2\sqrt{28}}$	$\frac{-1}{4\sqrt{14}}$	$\frac{-1}{4\sqrt{14}}$	-	$\frac{-1}{4}$	-	$\frac{-1}{4\sqrt{2}}$	$\frac{-1}{4\sqrt{30}}$	
FF	$\frac{1}{3}$	$\frac{1}{3}$	-	-	-	$\frac{1}{\sqrt{3}}$	-	-	-	-	-	-	$\frac{2}{3\sqrt{5}}$	$\frac{2}{3\sqrt{14}}$	-	-	-	$\frac{2}{\sqrt{42}}$	$\frac{3}{2\sqrt{70}}$	-	-	-	$\frac{1}{\sqrt{14}}$	-	-	$\frac{-1}{2\sqrt{2}}$	-	$\frac{-1}{2\sqrt{30}}$	
GG	-	-	-	-	-	-	-	-	-	-	-	-	$\frac{1}{\sqrt{5}}$	$\frac{-1}{\sqrt{14}}$	-	-	$\frac{3}{\sqrt{42}}$	-	$\frac{3}{8\sqrt{70}}$	-	-	$\frac{-1}{4\sqrt{14}}$	-	-	-	$\frac{1}{8\sqrt{2}}$	-	$\frac{1}{2\sqrt{30}}$	
GH	$\frac{1}{12}$	$\frac{-1}{6}$	-	-	-	$\frac{-1}{4\sqrt{3}}$	$\frac{3}{8\sqrt{3}}$	-	-	-	-	$\frac{1}{4\sqrt{2}}$	$\frac{13}{24\sqrt{5}}$	$\frac{-1}{3\sqrt{14}}$	-	-	-	$\frac{7}{4\sqrt{42}}$	$\frac{1}{8\sqrt{70}}$	-	-	-	-	-	-	$\frac{-1}{8\sqrt{2}}$	-	$\frac{-1}{4\sqrt{30}}$	
GI	$\frac{1}{12}$	$\frac{1}{12}$	$\frac{-1}{4\sqrt{3}}$	-	$\frac{1}{4\sqrt{3}}$	-	$\frac{3}{8\sqrt{3}}$	-	$\frac{1}{4\sqrt{2}}$	-	-	-	$\frac{13}{24\sqrt{5}}$	$\frac{1}{6\sqrt{14}}$	$\frac{7}{4\sqrt{42}}$	-	$\frac{1}{2\sqrt{42}}$	-	$\frac{-1}{2\sqrt{70}}$	-	-	$\frac{1}{4\sqrt{14}}$	-	-	-	-	-	$\frac{-1}{4\sqrt{30}}$	
HH	-	-	-	-	-	-	-	-	-	-	-	-	$\frac{1}{\sqrt{5}}$	$\frac{-1}{\sqrt{14}}$	-	-	$\frac{-3}{\sqrt{42}}$	-	$\frac{3}{8\sqrt{70}}$	-	-	$\frac{1}{4\sqrt{14}}$	-	-	-	$\frac{1}{8\sqrt{2}}$	-	$\frac{1}{2\sqrt{30}}$	
HI	$\frac{1}{12}$	$\frac{1}{12}$	-	$\frac{-1}{4\sqrt{3}}$	$\frac{-1}{4\sqrt{3}}$	-	$\frac{3}{8\sqrt{3}}$	-	-	$\frac{1}{4\sqrt{2}}$	-	-	$\frac{13}{24\sqrt{5}}$	$\frac{1}{6\sqrt{14}}$	-	$\frac{7}{4\sqrt{42}}$	$\frac{-1}{2\sqrt{42}}$	-	$\frac{-1}{2\sqrt{70}}$	-	-	$\frac{-1}{4\sqrt{14}}$	-	-	-	-	-	$\frac{-1}{4\sqrt{30}}$	
II	-	-	-	-	-	-	-	-	-	-	-	-	$\frac{1}{\sqrt{5}}$	$\frac{2}{\sqrt{14}}$	-	-	-	-	$\frac{1}{\sqrt{70}}$	-	-	-	-	-	-	-	-	$\frac{1}{2\sqrt{30}}$	

Table 7: Experimental Spectra → Spherical Basis $(F^{++}_{j_1 j_2 JM\Theta}(\underline{e}\,\underline{e}'))^{-}$

	XX	XY	XZ	XD	XE	XF	YY	YZ	YD	YE	YF	ZZ	ZD	ZE	ZF	DD	DE	DF	EE	EF	FF	GG	GH	GI	HH	HI	II
00 00	1	$\frac{2}{3}$	$\frac{2}{3}$	-	$-\frac{2}{3}$	$-\frac{2}{3}$	1	$\frac{2}{3}$	$-\frac{2}{3}$	-	$-\frac{2}{3}$	1	$-\frac{2}{3}$	$-\frac{2}{3}$	-	$\frac{2}{3}$	-	-	$\frac{2}{3}$	-	$\frac{2}{3}$	$-\frac{2}{3}$	-	-	$-\frac{2}{3}$	-	$-\frac{2}{3}$
02 20	$\frac{1}{2}$	$\frac{2}{3}$	$-\frac{1}{3}$	-	$\frac{1}{3}$	$-\frac{2}{3}$	$\frac{1}{2}$	$-\frac{1}{3}$	$\frac{1}{3}$	-	$-\frac{2}{3}$	-1	$\frac{1}{3}$	$\frac{1}{3}$	-	$-\frac{1}{3}$	-	-	$-\frac{1}{3}$	-	$\frac{2}{3}$	$\frac{1}{3}$	-	-	$\frac{1}{3}$	-	$-\frac{2}{3}$
02 21+	$\frac{1}{\sqrt{3}}$	-	$\frac{2}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$-\frac{2}{\sqrt{3}}$	-	-	-	$\frac{1}{\sqrt{3}}$	-	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	$-\frac{2}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	-	$-\frac{2}{\sqrt{3}}$	-	-	-	-	-	$-\frac{2}{\sqrt{3}}$	-	-	-
02 21-	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	$-\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$\frac{2}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	-	$-\frac{1}{\sqrt{3}}$	$\frac{2}{\sqrt{3}}$	-	$-\frac{1}{\sqrt{3}}$	-	-	-	-	$\frac{2}{\sqrt{3}}$	-	-	-	-	-	$-\frac{2}{\sqrt{3}}$	-
02 22+	$\frac{-3}{2\sqrt{3}}$	-	$-\frac{1}{\sqrt{3}}$	-	$\frac{1}{\sqrt{3}}$	-	$\frac{3}{2\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	-	-	-	$-\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	$\frac{1}{\sqrt{3}}$	-	-	$-\frac{1}{\sqrt{3}}$	-	-	$-\frac{1}{\sqrt{3}}$	-	-	$\frac{1}{\sqrt{3}}$	-	-
02 22-	$-\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	-	$\frac{2}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	$-\frac{1}{\sqrt{3}}$	$\frac{2}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	-	-	$\frac{2}{\sqrt{3}}$	-	-	-	-	-	$-\frac{2}{\sqrt{3}}$	-	-	-	-
11 00	-	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	$\frac{1}{\sqrt{3}}$	-	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	$-\frac{1}{\sqrt{3}}$	-	-	$-\frac{1}{\sqrt{3}}$	-	$-\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	-	-	$-\frac{1}{\sqrt{3}}$	-	$-\frac{1}{\sqrt{3}}$
11 20	-	$-\frac{2}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	-	$\frac{1}{\sqrt{6}}$	$-\frac{2}{\sqrt{6}}$	-	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	-	$-\frac{2}{\sqrt{6}}$	-	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	-	$-\frac{1}{\sqrt{6}}$	-	-	$-\frac{1}{\sqrt{6}}$	-	$\frac{2}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$	-	-	$-\frac{1}{\sqrt{6}}$	-	$\frac{2}{\sqrt{6}}$
11 21+	-	$-\frac{2}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-	-	$-\frac{1}{\sqrt{2}}$	$-\frac{2}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-	-	-	$\frac{1}{\sqrt{2}}$	-	-	$-\frac{2}{\sqrt{2}}$	-	-	-	-	$\frac{2}{\sqrt{2}}$	-	-	-
11 21-	-	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	$-\frac{2}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	-	-	-	$-\frac{1}{\sqrt{2}}$	-	-	-	-	$-\frac{1}{\sqrt{2}}$	-	-	-	-	$\frac{2}{\sqrt{2}}$	-	-	-	-	$\frac{2}{\sqrt{2}}$	-
11 22+	-	-	$\frac{1}{\sqrt{2}}$	-	$\frac{1}{\sqrt{2}}$	-	-	$-\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	-	-	-	$-\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-	$\frac{1}{\sqrt{2}}$	-	-	$-\frac{1}{\sqrt{2}}$	-	-	$\frac{1}{\sqrt{2}}$	-	-	$-\frac{1}{\sqrt{2}}$	-	-
11 22-	-	-	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	-	-	-	$\frac{1}{\sqrt{2}}$	-	$-\frac{1}{\sqrt{2}}$	-	-	$-\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	$-\frac{2}{\sqrt{2}}$	-	$\frac{2}{\sqrt{2}}$	-	-	-	-	-	$\frac{2}{\sqrt{2}}$	-	-	-	-
22 00	-	$\frac{1}{3\sqrt{5}}$	$\frac{1}{3\sqrt{5}}$	-	$-\frac{1}{3\sqrt{5}}$	$-\frac{1}{3\sqrt{5}}$	-	$\frac{1}{3\sqrt{5}}$	$-\frac{1}{3\sqrt{5}}$	-	$-\frac{1}{3\sqrt{5}}$	-	$-\frac{1}{3\sqrt{5}}$	$-\frac{1}{3\sqrt{5}}$	-	$\frac{1}{3\sqrt{5}}$	-	-	$\frac{1}{3\sqrt{5}}$	-	$\frac{1}{3\sqrt{5}}$	$\frac{5}{3\sqrt{5}}$	-	-	$\frac{5}{3\sqrt{5}}$	-	$\frac{5}{3\sqrt{5}}$
22 20	-	$\frac{-2}{3\sqrt{14}}$	$\frac{1}{3\sqrt{14}}$	-	$\frac{-1}{3\sqrt{14}}$	$\frac{2}{3\sqrt{14}}$	-	$\frac{1}{3\sqrt{14}}$	$\frac{-1}{3\sqrt{14}}$	-	$\frac{2}{3\sqrt{14}}$	-	$\frac{-1}{3\sqrt{14}}$	$\frac{-1}{3\sqrt{14}}$	-	$\frac{1}{3\sqrt{14}}$	-	-	$\frac{1}{3\sqrt{14}}$	-	$\frac{-2}{3\sqrt{14}}$	$\frac{-7}{3\sqrt{14}}$	-	-	$\frac{-7}{3\sqrt{14}}$	-	$\frac{14}{3\sqrt{14}}$
22 21+	$\frac{2}{\sqrt{42}}$	-	$\frac{1}{\sqrt{42}}$	$\frac{-1}{\sqrt{42}}$	$\frac{-4}{\sqrt{42}}$	-	$\frac{-3}{\sqrt{42}}$	-	$\frac{-1}{\sqrt{42}}$	$\frac{-6}{\sqrt{42}}$	$\frac{-1}{\sqrt{42}}$	$\frac{2}{\sqrt{42}}$	-	$\frac{-4}{\sqrt{42}}$	$\frac{-1}{\sqrt{42}}$	-	-	$\frac{2}{\sqrt{42}}$	-	-	-	-	-	$\frac{14}{\sqrt{42}}$	-	-	-
22 21-	$\frac{-4}{\sqrt{42}}$	$\frac{-7}{\sqrt{42}}$	$\frac{-7}{\sqrt{42}}$	$\frac{6}{\sqrt{42}}$	$\frac{1}{\sqrt{42}}$	$\frac{1}{\sqrt{42}}$	$\frac{-2}{\sqrt{42}}$	$\frac{-8}{\sqrt{42}}$	$\frac{4}{\sqrt{42}}$	$\frac{1}{\sqrt{42}}$	-	$\frac{-2}{\sqrt{42}}$	$\frac{4}{\sqrt{42}}$	-	$\frac{1}{\sqrt{42}}$	-	-	-	-	$\frac{-2}{\sqrt{42}}$	-	-	-	-	-	$\frac{14}{\sqrt{42}}$	-
22 22+	-	-	$\frac{1}{\sqrt{42}}$	-	$\frac{-1}{\sqrt{42}}$	-	-	$\frac{-1}{\sqrt{42}}$	$\frac{1}{\sqrt{42}}$	-	-	-	$\frac{1}{\sqrt{42}}$	$\frac{-1}{\sqrt{42}}$	-	$\frac{-1}{\sqrt{42}}$	-	-	$\frac{1}{\sqrt{42}}$	-	-	$\frac{7}{\sqrt{42}}$	-	-	$\frac{-7}{\sqrt{42}}$	-	-
22 22-	$\frac{-2}{\sqrt{42}}$	$\frac{-8}{\sqrt{42}}$	$\frac{-7}{\sqrt{42}}$	$\frac{1}{\sqrt{42}}$	-	$\frac{4}{\sqrt{42}}$	$\frac{-2}{\sqrt{42}}$	$\frac{-7}{\sqrt{42}}$	-	$\frac{1}{\sqrt{42}}$	$\frac{4}{\sqrt{42}}$	$\frac{-4}{\sqrt{42}}$	$\frac{1}{\sqrt{42}}$	$\frac{1}{\sqrt{42}}$	$\frac{6}{\sqrt{42}}$	-	$\frac{-2}{\sqrt{42}}$	-	-	-	-	-	$\frac{14}{\sqrt{42}}$	-	-	-	-
22 40	-	$\frac{2}{\sqrt{70}}$	$\frac{-8}{\sqrt{70}}$	-	$\frac{8}{\sqrt{70}}$	$\frac{-2}{\sqrt{70}}$	-	$\frac{-8}{\sqrt{70}}$	$\frac{8}{\sqrt{70}}$	-	$\frac{-2}{\sqrt{70}}$	-	$\frac{8}{\sqrt{70}}$	$\frac{8}{\sqrt{70}}$	-	$\frac{-8}{\sqrt{70}}$	-	-	$\frac{-8}{\sqrt{70}}$	-	$\frac{2}{\sqrt{70}}$	-	-	-	-	-	-
22 41+	$\frac{3}{\sqrt{28}}$	-	$\frac{-2}{\sqrt{28}}$	$\frac{2}{\sqrt{28}}$	$\frac{-6}{\sqrt{28}}$	-	$\frac{-1}{\sqrt{28}}$	-	$\frac{2}{\sqrt{28}}$	$\frac{-2}{\sqrt{28}}$	$\frac{2}{\sqrt{28}}$	$\frac{-4}{\sqrt{28}}$	-	$\frac{8}{\sqrt{28}}$	$\frac{2}{\sqrt{28}}$	-	-	$\frac{4}{\sqrt{28}}$	-	-	-	-	-	-	-	-	-
22 41-	$\frac{1}{\sqrt{28}}$	-	-	$\frac{2}{\sqrt{28}}$	$\frac{-2}{\sqrt{28}}$	$\frac{-2}{\sqrt{28}}$	$\frac{-3}{\sqrt{28}}$	$\frac{2}{\sqrt{28}}$	$\frac{6}{\sqrt{28}}$	$\frac{-2}{\sqrt{28}}$	-	$\frac{4}{\sqrt{28}}$	$\frac{-8}{\sqrt{28}}$	-	$\frac{-2}{\sqrt{28}}$	-	-	-	-	$\frac{4}{\sqrt{28}}$	-	-	-	-	-	-	-
22 42+	-	-	$\frac{4}{\sqrt{14}}$	-	$\frac{-4}{\sqrt{14}}$	-	-	$\frac{-4}{\sqrt{14}}$	$\frac{4}{\sqrt{14}}$	-	-	-	$\frac{4}{\sqrt{14}}$	$\frac{-4}{\sqrt{14}}$	-	$\frac{-4}{\sqrt{14}}$	-	-	$\frac{4}{\sqrt{14}}$	-	-	-	-	-	-	-	-
22 42-	$\frac{-1}{\sqrt{14}}$	$\frac{-4}{\sqrt{14}}$	-	$\frac{4}{\sqrt{14}}$	-	$\frac{2}{\sqrt{14}}$	$\frac{-1}{\sqrt{14}}$	-	-	$\frac{4}{\sqrt{14}}$	$\frac{2}{\sqrt{14}}$	$\frac{-2}{\sqrt{14}}$	$\frac{4}{\sqrt{14}}$	$\frac{4}{\sqrt{14}}$	$\frac{-4}{\sqrt{14}}$	-	$\frac{-8}{\sqrt{14}}$	-	-	-	-	-	-	-	-	-	-
22 43+	$\frac{-1}{2}$	-	-1	1	1	-	$\frac{-1}{2}$	-	1	-1	1	-	-	-	1	-	-	-2	-	-	-	-	-	-	-	-	-
22 43-	$\frac{-1}{2}$	-	-	-1	1	1	$\frac{-1}{2}$	-1	1	1	-	-	-	-	1	-	-	-	-	-2	-	-	-	-	-	-	-
22 44+	-	$\frac{-2}{\sqrt{2}}$	-	-	-	$\frac{2}{\sqrt{2}}$	-	-	-	-	$\frac{2}{\sqrt{2}}$	-	-	-	-	-	-	-	-	-	$\frac{-2}{\sqrt{2}}$	-	-	-	-	-	-
22 44-	$\frac{1}{\sqrt{2}}$	-	-	-	-	$\frac{-2}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	-	$\frac{2}{\sqrt{2}}$	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
a	-	$\frac{-4}{\sqrt{30}}$	$\frac{-4}{\sqrt{30}}$	-	$\frac{4}{\sqrt{30}}$	$\frac{4}{\sqrt{30}}$	-	$\frac{-4}{\sqrt{30}}$	$\frac{4}{\sqrt{30}}$	-	$\frac{4}{\sqrt{30}}$	-	$\frac{4}{\sqrt{30}}$	$\frac{4}{\sqrt{30}}$	-	$\frac{-4}{\sqrt{30}}$	-	-	$\frac{-4}{\sqrt{30}}$	-	$\frac{-4}{\sqrt{30}}$	-	-	-	-	-	-

Table 8: Cartesian Basis ↔ Point Group Basis $T^{\mu rr'\xi}_{\rho\rho'\sigma\sigma'++}$

C_2 , C_s , C_{2h}

$\rho\rho'\sigma\sigma'$	μ 0	0	0	0	0	0	0	0	0	0	0
	r 0	0	0	0	1	1	1	2	2	3	4
	r′ 0	1	2	3	1	2	3	2	3	3	4
xxxx	$\frac{1}{3}$	$\frac{-1}{3}$	-	$\frac{-1}{\sqrt{3}}$	$\frac{1}{6}$	-	$\frac{1}{\sqrt{6}}$	-	-	$\frac{1}{2}$	-
xxyy	$\frac{2}{3\sqrt{2}}$	$\frac{-2}{3\sqrt{2}}$	-	-	$\frac{1}{3\sqrt{2}}$	-	-	-	-	$\frac{-1}{\sqrt{2}}$	-
xxzz	$\frac{2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	-	$\frac{-1}{\sqrt{6}}$	$\frac{-2}{3\sqrt{2}}$	-	$\frac{-1}{\sqrt{3}}$	-	-	-	-
xxxy	-	-	$\frac{-1}{\sqrt{3}}$	-	-	$\frac{1}{\sqrt{6}}$	-	-	$\frac{-1}{\sqrt{2}}$	-	-
yyyy	$\frac{1}{3}$	$\frac{-1}{3}$	-	$\frac{1}{\sqrt{3}}$	$\frac{1}{6}$	-	$\frac{-1}{\sqrt{6}}$	-	-	$\frac{1}{2}$	-
yyzz	$\frac{2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	-	$\frac{1}{\sqrt{6}}$	$\frac{-2}{3\sqrt{2}}$	-	$\frac{1}{\sqrt{3}}$	-	-	-	-
yyxy	-	-	$\frac{-1}{\sqrt{3}}$	-	-	$\frac{1}{\sqrt{6}}$	-	-	$\frac{1}{\sqrt{2}}$	-	-
zzzz	$\frac{1}{3}$	$\frac{2}{3}$	-	-	$\frac{2}{3}$	-	-	-	-	-	-
zzxy	-	-	$\frac{-1}{\sqrt{3}}$	-	-	$\frac{-2}{\sqrt{6}}$	-	-	-	-	-
xyxy	-	-	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	-	-	$\frac{1}{\sqrt{2}}$
xyyx	-	-	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	-	-	$\frac{-1}{\sqrt{2}}$

	μ 1	1	1	1	1	1
	r 0	0	1	2	2	3
	r′ 0	1	1	2	3	3
yzyz	-	-	$\frac{1}{\sqrt{2}}$	-	-	$\frac{1}{\sqrt{2}}$
yzzy	-	-	$\frac{1}{\sqrt{2}}$	-	-	$\frac{-1}{\sqrt{2}}$
yzzx	-	$\frac{-1}{\sqrt{2}}$	-	-	$\frac{1}{\sqrt{2}}$	-
yzxz	-	$\frac{-1}{\sqrt{2}}$	-	-	$\frac{-1}{\sqrt{2}}$	-
zxzx	$\frac{1}{\sqrt{2}}$	-	-	$\frac{1}{\sqrt{2}}$	-	-
zxxz	$\frac{1}{\sqrt{2}}$	-	-	$\frac{-1}{\sqrt{2}}$	-	-

C_3 , C_{3_i}

$\rho\rho'\sigma\sigma'$	μ 0	0	0	0	1	1	1	1	1
	r 0	0	1	2	0	0_+	0_-	1	2
	r' 0	1	1	2	0	1^+	1^-	1	2
a_1	$\frac{2}{3\sqrt{2}}$	$\frac{-2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-	-	-	-	-
a_2	$\frac{2}{3\sqrt{2}}$	$\frac{-2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	-	-	-
zzzz	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	-	-	-	-	-	-
$xxzz^+$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{-2}{3}$	-	-	-	-	-	-
a_3	-	-	-	-	1	-	-	-	-
$xxzx^+$	-	-	-	-	-	1	-	-	-
$yyyz^+$	-	-	-	-	-	-	-1	-	-
$yzyz^+$	-	-	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$
$zxzx^+$	-	-	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$

$$xxzx^+ = \frac{1}{2}(xxzx - yyzx - xyyz - xyyz)$$
$$yyyz^+ = \frac{1}{2}(yyyz - xxyz - xyzx - xyxz)$$
$$yzyz^+ = \frac{1}{\sqrt{2}}(yzyz + yzzy)$$
$$zxzx^+ = \frac{1}{\sqrt{2}}(zxzx + zxxz)$$
$$xxzz^+ = \frac{1}{\sqrt{2}}(xxzz + yyzz)$$

YYYY = XXXX , YYZZ = XXZZ , XXYZ = XYZX = XYXZ = -(YYYZ) ,

ZXZX = YZYZ , ZXXZ = YZZY , YYZX = XYYZ = XYZY = -(XXZX) ,

XYYX = XXXX - XXYY - XYXY

C_4 , C_{4h} , S_4

$\rho\rho'\sigma\sigma'$	μ 0	0	0	0	2	2	2	1	1
	r 0	0	1	2	0	0	1	0	1
	r' 0	1	1	2	0	1	1	0	1
$xxxx^+$	$\frac{2}{3\sqrt{2}}$	$\frac{-2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	-	$\frac{1}{\sqrt{2}}$	-	-	-	-
xxyy	$\frac{2}{3\sqrt{2}}$	$\frac{-2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	-	$\frac{-1}{\sqrt{2}}$	-	-	-	-
$xxzz^+$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{-2}{3}$	-	-	-	-	-	-
zzzz	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	-	-	-	-	-	-
$xxxy^+$	-	-	-	-	-	-1	-	-	-
xyxy	-	-	-	$\frac{1}{\sqrt{2}}$	-	-	$\frac{1}{\sqrt{2}}$	-	-
xyyx	-	-	-	$\frac{-1}{\sqrt{2}}$	-	-	$\frac{1}{\sqrt{2}}$	-	-
$yzyz^+$	-	-	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$
$zxzx^+$	-	-	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$

$$xxxx^+ = \frac{1}{\sqrt{2}}(xxxx + yyyy)$$
$$xxzz^+ = \frac{1}{\sqrt{2}}(xxzz + yyzz)$$
$$xxxy^+ = \frac{1}{\sqrt{2}}(xxxy - yyxy)$$
$$yzyz^+ = \frac{1}{\sqrt{2}}(yzyz + yzzy)$$
$$zxzx^+ = \frac{1}{2}(zxzx + zxxz)$$

YYYY = XXXX

YYZZ = XXZZ

YYXY = - (XXXY)

ZXZX = YZYZ

ZXXZ = YZZY

C_6 , C_{6h} , C_{3h} (D_6 , C_{6v} , D_{3h} , D_{6h})

$\rho\rho'\,\sigma\sigma'$	μ r r′	0 0 0	0 0 1	0 1 1	0 2 2	(0 0 0)	2 0 0	1 0 0	1 1 1
a_1		$\frac{2}{3\sqrt{2}}$	$\frac{2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	$\frac{1}{\sqrt{2}}$		-	-	-
a_2		$\frac{2}{3\sqrt{2}}$	$\frac{2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$		-	-	-
zzzz		$\frac{1}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	-		-	-	-
$xxzz^+$		$\frac{2}{3}$	$\frac{-1}{3}$	$\frac{-2}{3}$	-		-	-	-
a_3		-	-	-	-		1	-	-
$yzyz^+$		-	-	-	-		-	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$
$zxzx^+$		-	-	-	-		-	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$

$$xxzz^+ = \frac{1}{\sqrt{2}}(xxzz + yyzz)$$

$$yzyz^+ = \frac{1}{\sqrt{2}}(yzyz + yzzy)$$

$$zxzx^+ = \frac{1}{\sqrt{2}}(zxzx + zxxz)$$

$$YYYY = XXXX\,,\quad YYZZ = XXZZ\,,\quad YZZY = ZXXZ$$

$$XYYX = XXXX - XXYY - XYXY\,,\quad ZXZX = YZYZ$$

D_2 , D_{2h} , C_{2v}

$\rho\rho'\,\sigma\sigma'$	μ r r′	0 0 0	0 0 1	0 0 2	0 1 1	0 1 2	0 2 2
xxxx		$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{-1}{\sqrt{3}}$	$\frac{1}{6}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{2}$
xxyy		$\frac{2}{3\sqrt{2}}$	$\frac{-2}{3\sqrt{2}}$	-	$\frac{1}{3\sqrt{2}}$	-	$\frac{-1}{\sqrt{2}}$
xxzz		$\frac{2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	$\frac{-1}{\sqrt{6}}$	$\frac{-2}{3\sqrt{2}}$	$\frac{-1}{\sqrt{3}}$	-
yyyy		$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{6}$	$\frac{-1}{\sqrt{6}}$	$\frac{1}{2}$
yyzz		$\frac{2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	$\frac{1}{\sqrt{6}}$	$\frac{-2}{3\sqrt{2}}$	$\frac{1}{\sqrt{3}}$	-
zzzz		$\frac{1}{3}$	$\frac{2}{3}$	-	$\frac{2}{3}$	-	-

$\rho\rho'\,\sigma\sigma'$	μ r r′	~ 0 0	~ 0 1	1 0 0	1 1 1	~ 1 0	~ 1 1
xyxy		$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-	-	-	-
xyyx		$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	-	-
yzyz		-	-	-	-	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$
yzzy		-	-	-	-	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$
zxzx		-	-	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-	-
zxxz		-	-	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-

D_3 , D_{3d} , C_{3v}

$\rho\rho'\sigma\sigma'$ \ μ r r′	0 0 0	0 0 1	0 1 1	1 0 0	1 0 1	1 1 1	1 2 2	$\tilde{0}$ 0 0
a_1	$\frac{2}{3\sqrt{2}}$	$\frac{-2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	-	-	-	-	$\frac{1}{\sqrt{2}}$
a_2	$\frac{2}{3\sqrt{2}}$	$\frac{-2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	-	-	-	-	$\frac{-1}{\sqrt{2}}$
$xxzz^+$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{-2}{3}$	-	-	-	-	-
zzzz	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	-	-	-	-	-
a_1	-	-	-	1	-	-	-	-
$xxzx^+$	-	-	-	-	1	-	-	-
$yzyz^+$	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-
$zxzx^+$	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-

$xxzz^+ = \frac{1}{\sqrt{2}}$ (xxzz + yyzz) $yzyz^+ = \frac{1}{\sqrt{2}}$ (yzyz + yzzy)

$zxzx^+ = \frac{1}{\sqrt{2}}$ (zxzx + zxxz) $xxzx^+ = \frac{1}{2}$ (xxzx-yyzx-xyyz-xyzy)

YYYY = XXXX,, YYZZ = XXZZ , ZXZX = YZYZ ,

ZXXZ = YZZY , XYYX = XXXX - XXYY - XYXY ,

YY2X = XYYZ = XYZY = -(XXZX)

D_4 , D_{4h} , C_{2v} , D_{2d}

$\rho\rho'\sigma\sigma'$ \ μ r r′	0 0 0	0 0 1	0 1 1	2 0 0	$\tilde{2}$ 0 0	1 0 0	1 1 1	$\tilde{1}$ 0 0
$xxxx^+$	$\frac{2}{3\sqrt{2}}$	$\frac{-2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-	-	-	-
xxyy	$\frac{2}{3\sqrt{2}}$	$\frac{-2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	-	-
$xxzz^+$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{-2}{3}$	-	-	-	-	-
zzzz	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	-	-	-	-	-
xyxy	-	-	-	-	$\frac{1}{\sqrt{2}}$	-	-	$\frac{1}{\sqrt{2}}$
xyyx	-	-	-	-	$\frac{1}{\sqrt{2}}$	-	-	$\frac{-1}{\sqrt{2}}$
$yzyz^+$	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-
$zxzx^+$	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-

$xxxx^+ = \frac{1}{\sqrt{2}}$ (xxxx + yyyy) $xxzz^+ = \frac{1}{\sqrt{2}}$ (xxzz + yyzz)

$yzyz^+ = \frac{1}{\sqrt{2}}$ (yzyz + yzzy) $zxzx^+ = \frac{1}{\sqrt{2}}$ (zxzx + zxxz)

YYYY = XXXX , YYZZ = XXZZ ,

ZXZX = YZYZ , YZZY = ZXXZ .

T , T_h , $(0$, 0_h , $T_d)$

$\rho\rho'\sigma\sigma'$	μ r r′	0 0 0	2 0 0	1 (1̃) 0 (0) 0 (0)	1 (1) 1 (0) 1 (0)
$xxxx^+$		$\frac{1}{\sqrt{3}}$	$\frac{2}{\sqrt{6}}$	-	-
$xxyy^+$		$\frac{2}{\sqrt{6}}$	$\frac{-1}{\sqrt{3}}$	-	-
$xyxy^+$		-	-	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$
$xyyx^+$		-	-	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$

$$xxxx^+ = \frac{1}{\sqrt{3}}\,(xxxx + yyyy + zzzz)$$

$$xxyy^+ = \frac{1}{\sqrt{3}}\,(xxyy + yyzz + zzxx)$$

$$xyxy^+ = \frac{1}{\sqrt{3}}\,(xyxy + yzyz + zxzx)$$

$$xyyx^+ = \frac{1}{\sqrt{3}}\,(xyyx + yzzy + zxxz)$$

$YYYY = ZZZZ = XXXX$, $XXYY = XXZZ = YYZZ$

$XYXY = YZYZ = ZXZX$, $XYYX = YZZY = ZXXZ$

K , R_3

$\rho\rho'\sigma\sigma'$	μ r r′	0 0 0	1 0 0	2 0 0
b_1		$\frac{3}{\sqrt{15}}$	$\frac{2}{\sqrt{10}}$	-
b_2		$\frac{1}{\sqrt{15}} - \frac{2}{\sqrt{30}}$	$\frac{1}{\sqrt{5}} - \frac{1}{\sqrt{10}}$	$\frac{1}{\sqrt{3}} + \frac{1}{\sqrt{6}}$
b_3		$\frac{1}{\sqrt{15}} + \frac{2}{\sqrt{30}}$	$\frac{-1}{\sqrt{5}} - \frac{1}{\sqrt{10}}$	$\frac{1}{\sqrt{3}} - \frac{1}{\sqrt{6}}$

$$b_1 = \frac{1}{\sqrt{5}}\,(xxxx^+ + \sqrt{2}\ xxyy^+ + xyxy^+ - xyyx^+)$$

$$b_2 = \frac{1}{\sqrt{5}}\,(xxxx^+ - xxyy^+ + \sqrt{2}\ xyxy^+ + xyyx^+)$$

$$b_3 = \frac{1}{\sqrt{5}}\,(xxxx^+ + xxyy^+ - xyxy^+ + \sqrt{2}\ xyyx^+)$$

with $xxxx^+$ etc. as for T.

$YYZZ = XXZZ = XXYY = XXXX - XYXY - XYYX$

$YYYY = ZZZZ = XXXX$, $ZXZX = YZYZ = XYXY$,

$ZXXZ = YZZY = XYYX$

Table 9: Experimental Spectra ← Point Group Basis $F^{++}_{\mu rr'\xi}(\underline{e}\ \underline{e}')$

C_2, C_s, C_{2h}																		
μ	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1
r	0	0	0	0	1	1	1	2	2	3	4	0	0	1	2	2	3
r′	0	1	2	3	1	2	3	2	3	3	4	0	1	1	2	3	3
β																	
XX	$\frac{1}{3}$	$\frac{-1}{3}$	-	$\frac{-1}{\sqrt{3}}$	$\frac{1}{6}$	-	$\frac{1}{\sqrt{6}}$	-	-	$\frac{1}{2}$	-	-	-	-	-	-	-
YY	$\frac{1}{3}$	$\frac{-1}{3}$	-	$\frac{1}{\sqrt{3}}$	$\frac{1}{6}$	-	$\frac{-1}{\sqrt{6}}$	-	-	$\frac{1}{2}$	-	-	-	-	-	-	-
ZZ	$\frac{1}{3}$	$\frac{2}{3}$	-	-	$\frac{2}{3}$	-	-	-	-	-	-	-	-	-	-	-	-
XY	-	-	-	-	-	-	-	$\frac{1}{2}$	-	-	$\frac{1}{2}$	-	-	-	-	-	-
XZ	-	-	-	-	-	-	-	-	-	-	-	$\frac{1}{2}$	-	-	$\frac{1}{2}$	-	-
YZ	-	-	-	-	-	-	-	-	-	-	-	-	-	$\frac{1}{2}$	-	-	$\frac{1}{2}$
XF	$\frac{1}{6}$	$\frac{-1}{6}$	$\frac{-1}{\sqrt{12}}$	$\frac{-1}{\sqrt{12}}$	$\frac{1}{12}$	$\frac{1}{2\sqrt{6}}$	$\frac{1}{2\sqrt{6}}$	$\frac{1}{4}$	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{4}$	$\frac{1}{4}$	-	-	-	-	-	-
YF	$\frac{1}{6}$	$\frac{-1}{6}$	$\frac{-1}{\sqrt{12}}$	$\frac{1}{\sqrt{12}}$	$\frac{1}{12}$	$\frac{1}{2\sqrt{6}}$	$\frac{-1}{2\sqrt{6}}$	$\frac{1}{4}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{4}$	$\frac{1}{4}$	-	-	-	-	-	-
EE	$\frac{1}{3}$	$\frac{1}{6}$	-	$\frac{-1}{\sqrt{12}}$	$\frac{1}{24}$	-	$\frac{-1}{4\sqrt{6}}$	-	-	$\frac{1}{8}$	-	$\frac{1}{2}$	-	-	-	-	-
HH	-	-	-	-	$\frac{3}{8}$	-	$\frac{3}{4\sqrt{6}}$	-	-	$\frac{1}{8}$	-	$\frac{1}{2}$	-	-	-	-	-
FF	$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{-1}{\sqrt{3}}$	-	$\frac{1}{6}$	$\frac{1}{\sqrt{6}}$	-	$\frac{1}{2}$	-	-	-	-	-	-	-	-	-
II	-	-	-	-	-	-	-	$\frac{1}{2}$	-	$\frac{1}{2}$	-	-	-	-	-	-	-
DD	$\frac{1}{3}$	$\frac{1}{6}$	-	$\frac{1}{\sqrt{12}}$	$\frac{1}{24}$	-	$\frac{1}{4\sqrt{6}}$	-	-	$\frac{1}{8}$	-	-	-	$\frac{1}{2}$	-	-	-
GG	-	-	-	-	$\frac{3}{8}$	-	$\frac{-3}{4\sqrt{6}}$	-	-	$\frac{1}{8}$	-	-	-	$\frac{1}{2}$	-	-	-
ZF	-	-	-	-	-	-	-	-	-	-	-	$\frac{1}{4}$	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{4}$
DE	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{-1}{2\sqrt{12}}$	-	$\frac{1}{6}$	$\frac{-1}{2\sqrt{6}}$	-	$\frac{1}{8}$	-	-	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{-1}{4\sqrt{2}}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{4\sqrt{2}}$	$\frac{1}{8}$
GH	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{1}{2\sqrt{12}}$	-	$\frac{1}{6}$	$\frac{1}{2\sqrt{6}}$	-	$\frac{1}{8}$	-	-	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{-1}{4\sqrt{2}}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{4\sqrt{2}}$	$\frac{1}{8}$

C_3 , C_{3i}

μ	0	0	0	0	1	1	1	1	1
r	0	0	1	2	0	0	1	1	2
r′	0	1	1	2	0	1	1-	1	2
β									
XX	$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{1}{6}$	-	$\frac{1}{2\sqrt{2}}$	-	-	-	-
ZZ	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	-	-	-	-	-	-
XY	-	-	-	$\frac{1}{2}$	$\frac{1}{2\sqrt{2}}$	-	-	-	-
XZ	-	-	-	-	-	-	-	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$
HH	-	-	$\frac{3}{8}$	-	$\frac{1}{8\sqrt{2}}$	-	-	$\frac{1}{2\sqrt{2}}$	-
II	-	-	-	-	$1/\sqrt{2}$	-	-	-	-
DD	$\frac{1}{3}$	$\frac{1}{6}$	$\frac{1}{24}$	-	$\frac{1}{8\sqrt{2}}$	-	$\frac{-1}{4}$	$\frac{1}{2\sqrt{2}}$	-
XD	-	-	-	$\frac{1}{4}$	$\frac{1}{4\sqrt{2}}$	-	$\frac{1}{4}$	$\frac{1}{4\sqrt{2}}$	$\frac{1}{4\sqrt{2}}$
YE	-	-	-	$\frac{1}{4}$	$\frac{1}{4\sqrt{2}}$	$\frac{-1}{4}$	-	$\frac{1}{4\sqrt{2}}$	$\frac{1}{4\sqrt{2}}$

C_4, C_{4h}, S_4

μ	0	0	0	0	2	2	2	1	1
r	0	0	1	2	0	0	1	0	1
r′	0	1	1	2	0	1	1	0	1
β									
XX	$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{1}{6}$	-	$\frac{1}{2}$	-	-	-	-
ZZ	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	-	-	-	-	-	-
XY	-	-	-	$\frac{1}{2}$	-	-	$\frac{1}{2}$	-	-
XZ	-	-	-	-	-	-	-	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$
XF	$\frac{1}{6}$	$\frac{-1}{6}$	$\frac{1}{12}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{4}$	-	-
EE	$\frac{1}{3}$	$\frac{1}{6}$	$\frac{1}{24}$	-	$\frac{1}{8}$	-	-	$\frac{1}{2\sqrt{2}}$	-
HH	-	-	$\frac{3}{8}$	-	$\frac{1}{8}$	-	-	$\frac{1}{2\sqrt{2}}$	-
FF	$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{1}{6}$	-	-	-	$\frac{1}{2}$	-	-
II	-	-	-	-	$\frac{1}{2}$	-	$\frac{1}{2}$	-	-

C_6, C_{6h}, C_{3h} (D_6, D_{3h}, D_{6h}, C_{6v})

	μ	0	0	0	2	1	1	0	$\begin{pmatrix}\tilde{0}\\0\\0\end{pmatrix}$
	r	0	0	1	0	0	1	2	
β	r′	0	1	1	0	0	1	2	
XX		$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{6}$	$\frac{1}{2\sqrt{2}}$	-	-	-	
ZZ		$\frac{1}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	-	-	-	-	
XY		-	-	-	$\frac{1}{2\sqrt{2}}$	-	-	$\frac{1}{2}$	
XZ		-	-	-	-	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	-	
EE		$\frac{1}{3}$	$\frac{-1}{6}$	$\frac{1}{24}$	$\frac{1}{8\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	-	-	
HH		-	-	$\frac{3}{8}$	$\frac{1}{8\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	-	-	
II		-	-	-	$\frac{1}{\sqrt{2}}$	-	-	-	

D_2, D_{2h}, C_{2v}

	μ	0	0	0	0	0	0	$\tilde{0}$	$\tilde{0}$	1	1	$\tilde{1}$	$\tilde{1}$
	r	0	0	0	1	1	2	0	1	0	1	0	1
β	r′	0	1	2	1	2	2	0	1	0	1	0	1
XX		$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{-1}{\sqrt{3}}$	$\frac{1}{6}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{2}$	-	-	-	-	-	-
YY		$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{6}$	$\frac{-1}{\sqrt{6}}$	$\frac{1}{2}$	-	-	-	-	-	-
ZZ		$\frac{1}{3}$	$\frac{2}{3}$	-	$\frac{2}{3}$	-	-	-	-	-	-	-	-
XY		-	-	-	-	-	-	$\frac{1}{2}$	$\frac{1}{2}$	-	-	-	-
XZ		-	-	-	-	-	-	-	-	$\frac{1}{2}$	$\frac{1}{2}$	-	-
YZ		-	-	-	-	-	-	-	-	-	-	$\frac{1}{2}$	$\frac{1}{2}$
EE		$\frac{1}{3}$	$\frac{1}{6}$	$\frac{-1}{\sqrt{12}}$	$\frac{1}{24}$	$\frac{-1}{4\sqrt{6}}$	$\frac{1}{8}$	-	-	$\frac{1}{2}$	-	-	-
HH		-	-	-	$\frac{3}{8}$	$\frac{3}{4\sqrt{6}}$	$\frac{1}{8}$	-	-	$\frac{1}{2}$	-	-	-
FF		$\frac{1}{3}$	$\frac{-1}{3}$	-	$\frac{1}{6}$	-	-	$\frac{1}{2}$	-	-	-	-	-
II		-	-	-	-	-	$\frac{1}{2}$	$\frac{1}{2}$	-	-	-	-	-
DD		$\frac{1}{3}$	$\frac{1}{6}$	$\frac{1}{\sqrt{12}}$	$\frac{1}{24}$	$\frac{1}{4\sqrt{6}}$	$\frac{1}{8}$	-	-	-	-	$\frac{1}{2}$	-
GG		-	-	-	$\frac{3}{8}$	$\frac{-3}{4\sqrt{6}}$	$\frac{1}{8}$	-	-	-	-	$\frac{1}{2}$	

D_3, C_{3v}, D_{3d}

β \ μ	0	0	0	1	1	1	1	$\tilde{0}$
r	0	0	1	0	0	1	2	0
r′	0	1	1	0	1	1	2	0
XX	$\frac{1}{3}$	$-\frac{1}{3}$	$\frac{1}{6}$	$\frac{1}{2\sqrt{2}}$	-	-	-	-
ZZ	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	-	-	-	-	-
XY	-	-	-	$\frac{1}{2\sqrt{2}}$	-	-	-	$\frac{1}{2}$
XZ	-	-	-	-	-	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	-
HH	-	-	$\frac{3}{8}$	$\frac{1}{8\sqrt{2}}$	-	$\frac{1}{8\sqrt{2}}$	-	-
II	-	-	-	$1/\sqrt{2}$	-	-	-	-
DD	$\frac{1}{3}$	$\frac{1}{6}$	$\frac{1}{24}$	$\frac{1}{8\sqrt{2}}$	-	$\frac{1}{2\sqrt{2}}$	-	-
YE	-	-	-	$\frac{1}{4\sqrt{2}}$	$-\frac{1}{4}$	$\frac{1}{4\sqrt{2}}$	$\frac{1}{4\sqrt{2}}$	$\frac{1}{4}$

D_4, D_{2d}, D_{4h}, C_{4v}

β \ μ	0	0	0	2	$\tilde{2}$	1	1	$\tilde{0}$
r	0	0	1	0	0	0	1	0
r′	0	1	1	0	0	0	1	0
XX	$\frac{1}{3}$	$-\frac{1}{3}$	$\frac{1}{6}$	$\frac{1}{2}$	-	-	-	-
ZZ	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	-	-	-	-	-
XY	-	-	-	-	$\frac{1}{2}$	-	-	$\frac{1}{2}$
XZ	-	-	-	-	-	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	-
EE	$\frac{1}{3}$	$\frac{1}{6}$	$\frac{1}{24}$	$\frac{1}{8}$	-	$\frac{1}{2\sqrt{2}}$	-	-
HH	-	-	$\frac{3}{8}$	$\frac{1}{8}$	-	$\frac{1}{2\sqrt{2}}$	-	-
FF	$\frac{1}{3}$	$-\frac{1}{3}$	$\frac{1}{6}$	-	$\frac{1}{2}$	-	-	-
II	-	-	-	$\frac{1}{2}$	$\frac{1}{2}$	-	-	-

		O,	O_h,	T_d $(T,$	$T_h)$
	μ	0	2	$\mathfrak{T}\begin{pmatrix}1\\0\end{pmatrix}$	$1\begin{pmatrix}1\\0\end{pmatrix}$
	r	0	0	$0\begin{pmatrix}0\\1\end{pmatrix}$	$0\begin{pmatrix}1\\1\end{pmatrix}$
	r'	0	0	$0\begin{pmatrix}0\\1\end{pmatrix}$	$0\begin{pmatrix}1\\1\end{pmatrix}$
β					
XX		$\frac{1}{3}$	$\frac{\sqrt{2}}{3}$	-	-
XY		-	-	$\frac{1}{2\sqrt{3}}$	$\frac{1}{2\sqrt{3}}$
HH		-	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{3}}$	-
DD		$\frac{1}{3}$	$\frac{1}{6\sqrt{2}}$	$\frac{1}{2\sqrt{3}}$	-

		K,	R_3	
	μ	0	1	2
	r	0	0	0
	r'	0	0	0
β				
XX		$\frac{1}{3}$	-	$\frac{2}{3\sqrt{5}}$
XY		-	$\frac{1}{2\sqrt{3}}$	$\frac{1}{2\sqrt{5}}$
HH		-	-	$\frac{1}{\sqrt{5}}$

Table 10: Experimental Spectra → Point Group Basis $(F^{++}_{\mu rr',\xi}(\underline{e}\,\underline{e}'))^{-1}$

C_2, C_s, C_{2h}

$\mu rr'$ \ β	XX	YY	ZZ	XY	XZ	YZ	XF	YF	EE	HH	FF	II	DD	GG	ZF	DE	GH
000	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{2}{3}$	-	-	$\frac{-2}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{-2}{3}$	-	-	-
001	$\frac{-2}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{-2}{3}$	-	-	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{-1}{3}$	-	-	-
002	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	$\frac{2}{\sqrt{3}}$	-	-	$\frac{-2}{\sqrt{3}}$	$\frac{-2}{\sqrt{3}}$	-	-	-	-	-	-	-	$\frac{-2}{\sqrt{3}}$	$\frac{2}{\sqrt{3}}$
003	$\frac{-1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	-	-	-	-	-	$\frac{-1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	-	$\frac{1}{\sqrt{3}}$	$\frac{-1}{\sqrt{3}}$	-	-	-
011	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	-	-	$\frac{-1}{3}$	$\frac{-1}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	-	-	-
012	$\frac{-1}{\sqrt{6}}$	$\frac{-1}{\sqrt{6}}$	-	$\frac{-2}{\sqrt{6}}$	-	-	$\frac{2}{\sqrt{6}}$	$\frac{2}{\sqrt{6}}$	-	-	-	-	-	-	-	$\frac{-4}{\sqrt{6}}$	$\frac{4}{\sqrt{6}}$
013	$\frac{1}{\sqrt{6}}$	$\frac{-1}{\sqrt{6}}$	-	-	-	-	-	-	$\frac{-2}{\sqrt{6}}$	$\frac{2}{\sqrt{6}}$	-	-	$\frac{-2}{\sqrt{6}}$	$\frac{-2}{\sqrt{6}}$	-	-	-
022	-	-	-	1	-	-	-1	-1	-	-	1	1	-	-	-	-	-
023	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	-	-	$-\sqrt{2}$	$\sqrt{2}$	-	-	-	-	-	-	-	-	-
033	-	-	-	-1	-	-	1	1	-	-	-1	1	-	-	-	-	-
044	-	-	-	1	-	-	1	1	-	-	-1	-1	-	-	-	-	-
100	$\frac{-1}{2}$	-	$\frac{-1}{2}$	-	-	-	-	-	1	1	-	-	-	-	-	-	-
101	-	-	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	$\sqrt{2}$	$\sqrt{2}$	-	-	-	-	-	-	-	-	$-\sqrt{2}$	$-\sqrt{2}$	$-\sqrt{2}$
111	-	$\frac{-1}{2}$	$\frac{-1}{2}$	-	-	-	-	-	-	-	-	-	1	1	-	-	-
122	$\frac{1}{2}$	-	$\frac{1}{2}$	-	2	-	-	-	-1	-1	-	-	-	-	-	-	-
123	-	-	$\frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	-	-	-	-	-	-	-	-	$-\sqrt{2}$	$\sqrt{2}$	$\sqrt{2}$
133	-	$\frac{1}{2}$	$\frac{1}{2}$	-	-	2	-	-	-	-	-	-	-1	-1	-	-	-

C_3, C_{3i}

μrr′ \ β	XX	ZZ	XY	XZ	HH	II	DD	XD	YE
000	$\frac{4}{3}$	$\frac{1}{3}$	$-\frac{2}{3}$	$-\frac{2}{3}$	$-\frac{4}{3}$	$-\frac{2}{3}$	$\frac{4}{3}$	$\frac{4}{3}$	-
001	$-\frac{4}{3}$	$\frac{2}{3}$	$-\frac{1}{3}$	$-\frac{1}{3}$	$-\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	-
011	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{4}{3}$	$-\frac{1}{3}$	$-\frac{4}{3}$	$-\frac{4}{3}$	-
022	-	-	2	-	-	-1	-	-	-
100	-	-	-	-	-	$\sqrt{2}$	-	-	-
101	-	-	2	2	-	-	-	-	-4
110	-	-	-2	-2	-	-	-	4	-
111	$\frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	$\sqrt{2}$	-	$\sqrt{2}$	$\sqrt{2}$	-
122	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	$\frac{5}{\sqrt{2}}$	$-\sqrt{2}$	-	$-\sqrt{2}$	$-\sqrt{2}$	-

C_4, C_{4h}, S_4

μrr′ \ β	XX	ZZ	XY	XZ	XF	EE	HH	FF	II
000	$\frac{2}{3}$	$\frac{1}{3}$	-	-	-	$\frac{4}{3}$	$-\frac{4}{3}$	$\frac{2}{3}$	$-\frac{2}{3}$
001	$-\frac{2}{3}$	$\frac{2}{3}$	-	-	-	$\frac{2}{3}$	$-\frac{2}{3}$	$-\frac{2}{3}$	$\frac{2}{3}$
011	$\frac{1}{3}$	$\frac{2}{3}$	-	-	-	$-\frac{4}{3}$	$\frac{4}{3}$	$\frac{1}{3}$	$-\frac{1}{3}$
022	1	-	2	-	-	-	-	-1	-1
200	1	-	-	-	-	-	-	-1	1
201	$\sqrt{2}$	-	$\sqrt{2}$	-	$-2\sqrt{2}$	-	-	-	-
211	-1	-	-	-	-	-	-	1	1
100	$\frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	-	$\sqrt{2}$	$\sqrt{2}$	-	-
111	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-	$2\sqrt{2}$	-	$-\sqrt{2}$	$-\sqrt{2}$	-	-

C_6, C_{6h}, C_{3h}, $(D_6, D_{3h}, D_{6h}, C_{6v})$

$\mu rr'$ \ β	XX	ZZ	XY	XZ	EE	HH	II
000	$\frac{4}{3}$	$\frac{1}{3}$	-	-	$\frac{4}{3}$	$\frac{-4}{3}$	$\frac{-2}{3}$
001	$\frac{4}{3}$	$\frac{-2}{3}$	-	-	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{-2}{3}$
011	$\frac{2}{3}$	$\frac{2}{3}$	-	-	$\frac{-4}{3}$	$\frac{4}{3}$	$\frac{-1}{3}$
200	-	-	-	-	-	-	$\sqrt{2}$
100	$\frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	$\sqrt{2}$	$\sqrt{2}$	-
111	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-	$2\sqrt{2}$	$-\sqrt{2}$	$-\sqrt{2}$	-
$\tilde{(000)}022$	-	-	2	-	-	-	-1

D_2, D_{2h}, C_{2v}

$\mu rr'$ \ β	XX	YY	ZZ	XY	XZ	YZ	EE	HH	FF	II	DD	GG
000	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	-	-	-	$\frac{2}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{-2}{3}$
001	$\frac{-1}{3}$	$\frac{-1}{3}$	$\frac{2}{3}$	-	-	-	$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{-1}{3}$
002	$\frac{-1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	-	-	-	$\frac{-1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	-	$\frac{1}{\sqrt{3}}$	$\frac{-1}{\sqrt{3}}$
011	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{2}{3}$	-	-	-	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$
012	$\frac{1}{\sqrt{6}}$	$\frac{-1}{\sqrt{6}}$	-	-	-	-	$\frac{-2}{\sqrt{6}}$	$\frac{2}{\sqrt{6}}$	-	-	$\frac{2}{\sqrt{6}}$	$\frac{-2}{\sqrt{6}}$
022	$\frac{1}{2}$	$\frac{1}{2}$	-	-	-	-	-	-	-1	1	-	-
$\tilde{000}$	$\frac{-1}{2}$	$\frac{-1}{2}$	-	-	-	-	-	-	1	1	-	-
$\tilde{011}$	$\frac{1}{2}$	$\frac{1}{2}$	-	2	-	-	-	-	-1	-1	-	-
100	$\frac{-1}{2}$	-	$\frac{-1}{2}$	-	-	-	1	1	-	-	-	-
111	$\frac{1}{2}$	-	$\frac{1}{2}$	-	2	-	-1	-1	-	-	-	-
$\tilde{100}$	-	$\frac{-1}{2}$	$\frac{-1}{2}$	-	-	-	-	-	-	-	1	1
$\tilde{111}$	-	$\frac{1}{2}$	$\frac{1}{2}$	-	-	2	-	-	-	-	-1	-1

D_3, C_{3v}, D_{3d}

$\mu rr'$ \ β	XX	ZZ	XY	XZ	HH	II	DD	YE
000	$\frac{4}{3}$	$\frac{1}{3}$	-	-	$\frac{-4}{3}$	$\frac{-2}{3}$	$\frac{4}{3}$	-
001	$\frac{-4}{3}$	$\frac{2}{3}$	-	-	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	-
011	$\frac{2}{3}$	$\frac{2}{3}$	-	-	$\frac{4}{3}$	$\frac{-1}{3}$	$\frac{-4}{3}$	-
100	-	-	-	-	-	$\sqrt{2}$	-	-
101	-	-	2	2	-	-	-	-4
111	$\frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	$\sqrt{2}$	-	$\sqrt{2}$	-
122	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-	$2\sqrt{2}$	$-\sqrt{2}$	-	$-\sqrt{2}$	-
~ 000	-	-	2	-	-	-1	-	-

$D_4, D_{2d}, D_{4h}, C_{4v}$

$\mu rr'$ \ β	XX	ZZ	XY	XZ	EE	HH	FF	II
000	$\frac{2}{3}$	$\frac{1}{3}$	-	-	$\frac{4}{3}$	$\frac{-4}{3}$	$\frac{2}{3}$	$\frac{-2}{3}$
001	$\frac{-2}{3}$	$\frac{2}{3}$	-	-	$\frac{2}{3}$	$\frac{-2}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$
011	$\frac{1}{3}$	$\frac{2}{3}$	-	-	$\frac{-4}{3}$	$\frac{4}{3}$	$\frac{1}{3}$	$\frac{-1}{3}$
200	1	-	-	-	-	-	-1	1
~ 200	-1	-	-	-	-	-	1	1
100	$\frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	$\sqrt{2}$	$\sqrt{2}$	-	-
111	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-	$2\sqrt{2}$	$-\sqrt{2}$	$-\sqrt{2}$	-	-
~ 000	1	-	2	-	-	-	-1	-1

$O, O_h, T_d, (T, T_h)$

$\mu rr'$ \ β	XX	XY	HH	DD
000	1	-	-2	2
200	$\sqrt{2}$	-	$\sqrt{2}$	$-\sqrt{2}$
(100) 100	$-\sqrt{3}$	-	$\sqrt{3}$	$\sqrt{3}$
(111) 100	$\sqrt{3}$	$2\sqrt{3}$	$-\sqrt{3}$	$-\sqrt{3}$

K, R_3

$\mu rr'$ \ β	XX	XY	HH
000	3	-	-2
100	-	$2\sqrt{3}$	$-\sqrt{3}$
200	-	-	$\sqrt{5}$

Table 11: Linear Relationships Among Intensity Measurements

Relationships among the scattering intensities for a real symmetric scatterer ($\eta = \varepsilon = {}^{+}1$) in all point groups. AB represents the scattering intensity for incident/scattered light with unit polarisation vector A/B* or absorption coefficient for two photons A,B.

C_2, C_s, C_{2h}

$XE = \frac{1}{2}(XX + XZ)$, $YD = \frac{1}{2}(YY + YZ)$, $ZE = \frac{1}{2}(ZZ + XZ)$,
$ZD = \frac{1}{2}(ZZ + YZ)$, $XD = \frac{1}{2}(XY + XZ)$, $YE = \frac{1}{2}(XY + YZ)$,
$DF = \frac{1}{2}(YF + ZF)$, $EF = \frac{1}{2}(XF + ZF)$,
$GI = \frac{1}{4}(YY + XY + XZ + YZ)$, $HI = \frac{1}{4}(XX + XY + XZ + YZ)$.

C_3, C_{3i}

$XF = YF = \frac{1}{2}(XX + XY)$, $DF = \frac{1}{4}(XX + 4YE - XY)$,
$XE = \frac{1}{2}(XX + XY + 2XZ - 2YE)$, $GI = HI = \frac{1}{4}(XX + XY + 2XZ)$,
$YD = \frac{1}{2}(XX - 2XD + XY + XZ)$, $EF = \frac{1}{4}(XX + 4XD - XY)$,
$ZE = ZD = \frac{1}{2}(ZZ + XZ)$, $DE = \frac{1}{4}(ZZ + 2XD + 2YE - XY)$,
$EE = DD - YE + XD$, $GH = \frac{1}{4}(ZZ + XY + 2XZ)$,
$YY = FF = XX$, $YZ = ZF = XZ$, $HH = GG$.

C_4, C_{4h}, S_4

$YD = XE = \frac{1}{2}(XX + XZ)$, $YF = (XX + XY - XF)$,
$ZE = ZD = \frac{1}{2}(ZZ + XZ)$, $GI = HI = \frac{1}{4}(XX + XY + 2XZ)$,
$XD = YE = \frac{1}{2}(XY + XZ)$, $DE = GH = \frac{1}{4}(ZZ + XY + 2XZ)$,
$DF = \frac{1}{2}(YF + XZ)$, $YY = XX$,
$EF = \frac{1}{2}(XF + XZ)$, $YZ = ZF = XZ$,
$GG = HH$, $DD = EE$.

C_6, C_{6h}, C_{3h} ; D_6, D_{3h}, D_{6h}, C_{6v}

$XE = YD = \frac{1}{2}(XX + XZ)$, $XD = YE = \frac{1}{2}(XY + XZ)$,
$XF = YF = \frac{1}{2}(XX + XY)$, $DF = GI = EF = HI = \frac{1}{4}(XX + XY + 2XZ)$,
$ZE = ZD = \frac{1}{2}(ZZ + XZ)$, $GH = DE = \frac{1}{4}(ZZ + XY + 2XZ)$,
$YY = FF = XX$, $YZ = ZF = XZ$, $DD = EE$, $HH = GG$.

D_2, D_{2h}, C_{2v}

$XE = \frac{1}{2}(XX + XZ)$, $XD = \frac{1}{2}(XY + XZ)$,

$XF = \frac{1}{2}(XX + XY)$, $YE = \frac{1}{2}(XY + YZ)$,

$YD = \frac{1}{2}(YY + YZ)$, $ZF = \frac{1}{2}(XZ + YZ)$,

$YF = \frac{1}{2}(YY + XY)$, $DF = GI = \frac{1}{4}(XX + XY + XZ + YZ)$,

$ZE = \frac{1}{2}(ZZ + XZ)$, $EF = HI = \frac{1}{4}(YY + XY + XZ + YZ)$,

$ZD = \frac{1}{2}(ZZ + YZ)$, $DE = GH = \frac{1}{4}(ZZ + XY + XZ + YZ)$.

D_3, C_{3v}, D_{3d}

$YY = FF = XX$, $YZ = ZF = XZ$, $HH = GG$,

$XE = \frac{1}{2}(XX - 2YE + 2XZ + XY)$, $XD = \frac{1}{2}(XY + XZ)$,

$XF = YF = \frac{1}{2}(XX + XY)$, $DF = \frac{1}{4}(XX + 4YE - XY)$,

$YD = \frac{1}{2}(XX + XZ)$, $GI = EF = HI =$

$ZD = ZE = \frac{1}{2}(ZZ + XZ)$, $\frac{1}{4}(XX + XY + 2XZ)$,

$EE = \frac{1}{2}(2DD - 2YE + XZ + XY)$, $GH = \frac{1}{4}(ZZ + XY + 2XZ)$,

$DE = \frac{1}{4}(ZZ + 2YE + XZ)$.

D_4, D_{2d}, D_{4h}, C_{4v}

$XE = YD = \frac{1}{2}(XX + XZ)$, $XD = YE = \frac{1}{2}(XY + XZ)$,

$XF = YF = \frac{1}{2}(XX + XY)$, $DF = GI = EF = HI = \frac{1}{4}(XX + XY + 2XZ)$,

$ZE = ZD = \frac{1}{2}(ZZ + XZ)$, $DE = GH = \frac{1}{4}(ZZ + XY + 2XZ)$,

$YY = XX$, $YZ = ZF = XZ$, $DD = EE$, $GG = HH$.

O, O_h, T, T_d T_h

$XE = XF = YD = YF = ZE = ZD = \frac{1}{2}(XX + XY)$,

$DF = HI = EF = GI = DE = GH = \frac{1}{4}(XX + 3XY)$,

$YY = ZZ = XX$, $XZ = YZ = XD = YE = ZF = XY$,

$EE = FF = DD$, $HH = II = GG$.

K, R_3

$XE = XF = YD = YF = ZE = ZD = \frac{1}{2}(XX + XY)$,

$DF = HI = EF = GI = DE = GH = \frac{1}{4}(XX + 3XY)$,

$YY = ZZ = DD = EE = FF = XX$,

$XZ = YZ = XD = YE = ZF = XY$,

$II = HH = GG$.

Table 12: Selection Rules for Phonon Raman Effect: Oriented Scatterers

Constants $c_{\mu rr'}$, which contribute to the Raman spectrum for electronic ground state Λ and phonon symmetry κ. All non degenerate ground states $|\Lambda| = 1$ are included in the rows $\Lambda = 0$. An asterisk indicates that the constants are factorisable (equation 3.29).

C_2, C_s, C_{2h}

	$\mu=$	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1
	$r=$	0	0	0	1	1	1	2	2	3	4	0	0	1	2	2	3
	$r'=$	0	1	2	1	2	3	2	3	3	4	0	1	1	2	3	3
Λ	κ																
0	0	1*	1*	1*	1*	1*	1*	1*	1*	1*	1*	—	—	—	—	—	—
	1	—	—	—	—	—	—	—	—	—	—	1*	1*	1*	—	—	—
$\pm\frac{1}{2}$	0	1*	1*	1*	1*	1*	1*	1*	1*	1*	1*	—	—	—	1	1	1
	1	—	—	—	—	—	—	—	—	—	1	1*	1*	1*	1	1	1

C_3, C_{3i}

	$\mu=$	0	0	0	0	1	1	1	1	1
	$r=$	0	0	1	2	0	0	1	1	2
	$r'=$	0	1	1	2	0	1	0	1	2
Λ	κ									
0	0	1*	1*	1*	—	—	—	—	—	—
	±1	—	—	—	—	1*	1*	1*	1*	—
$\pm\frac{1}{2}$	0	1*	1*	1*	1*	—	—	—	—	1*
	±1	—	—	—	1	1*	1*	1*	1*	1
±1	0	1*	1*	1*	1*	1*	1*	1*	1*	—
	±1	1	1	1	—	1	1	1	1	1*

C_4, C_{4h}, S_4

	$\mu=$	0	0	0	0	2	2	2	1	1
	$r=$	0	0	1	2	0	0	1	0	1
	$r'=$	0	1	1	2	0	1	1	0	1
Λ	κ									
0	0	1*	1*	1*	—	—	—	—	—	—
	±1	—	—	—	—	—	—	—	1*	—
	2	—	—	—	—	1*	1*	1*	—	—
$\pm\frac{1}{2}, \pm\frac{3}{2}$	0	1*	1*	1*	1*	—	—	—	—	1*
	±1	—	—	—	1	—	—	—	1*	1
	2	—	—	—	—	1*	1*	1*	—	1*
±1	0	1*	1*	1*	1*	1	1	1	—	—
	±1	—	—	—	—	—	—	—	1	1*
	2	1	1	1	—	1	1	1	—	—

C_6, C_{6h}, C_{3h}

		$\mu=$	0	0	0	0	2	1	1
		$r=$	0	0	1	2	0	0	1
		$r'=$	0	1	1	2	0	0	1
Λ	κ								
0	0		1*	1*	1*	—	—	—	—
	±1		—	—	—	—	—	1*	—
	±2		—	—	—	—	1*	—	—
±½, ±3/2	0		1*	1*	1*	1*	—	—	1*
	±1		—	—	—	1	—	1*	1
	±2		—	—	—	—	1*	—	1*
±1, ±2	0		1*	1*	1*	1*	1*	—	—
	±1		—	—	—	—	—	1	1*
	±2		1	1	1	—	1	—	—
	3		—	—	—	—	—	1*	—
±3/2	0		1*	1*	1*	1*	—	—	—
	±1		—	—	—	—	—	1*	1*
	±2		—	—	—	—	1*	—	1
	3		—	—	—	1	—	—	—

D_2, D_{2h}, C_{2v}

	$\mu=0$	0	0	0	0	0	$\bar{0}$	$\bar{0}$	1	1	$\bar{1}$	$\bar{1}$
	$r=0$	0	0	1	1	2	0	1	0	1	0	1
	$r'=0$	1	2	1	2	2	0	1	0	1	0	1
Λ	κ											
0	0	1*	1*	1*	1*	1*	1*	—	—	—	—	—	—
	$\bar{0}$	—	—	—	—	—	—	1*	—	—	—	—	—
	1	—	—	—	—	—	—	—	—	1*	—	—	—
	$\bar{1}$	—	—	—	—	—	—	—	—	—	—	1*	—
½	0	1*	1*	1*	1*	1*	1*	—	1*	—	1*	—	1*
	$\bar{0}$	—	—	—	—	—	—	1*	—	—	1*	—	1*
	1	—	—	—	—	—	—	—	1*	1*	—	—	1*
	$\bar{1}$	—	—	—	—	—	—	—	1*	—	1*	1*	—

D_3, C_{3v}, D_{3d}

	$\mu=$	0	0	0	1	1	1	1	$\bar{0}$
	$r=$	0	0	1	0	0	1	2	0
	$r'=$	0	1	1	0	1	1	2	0
Λ	κ								
0	0	1*	1*	1*	—	—	—	—	—
	1	—	—	—	1*	1*	1*	—	—
½	0	1*	1*	1*	—	—	—	1*	1*
	$\bar{0}$	—	—	—	—	—	—	1*	—
	1	—	—	—	1*	1*	1*	1	1*
1	0	1*	1*	1*	1*	1*	1*	—	1*
	$\bar{0}$	—	—	—	1*	1*	1*	—	—
	1	1*	1*	1*	1	1	1	1*	—
±3/2	0	1*	1*	1*	—	—	—	—	1
	$\bar{0}$	—	—	—	—	—	—	—	1
	1	—	—	—	1*	1*	1*	1	—

D_4, D_{2d}, D_{4h}, C_{4v}

	$\mu=$	0	0	0	2	$\bar{2}$	1	1	$\bar{0}$
	$r=$	0	0	1	0	0	0	1	0
	$r'=$	0	1	1	0	0	0	1	0
Λ	κ								
0	0	1*	1*	1*	—	—	—	—	—
	1	—	—	—	—	—	1*	—	—
	2	—	—	—	1*	—	—	—	—
	$\bar{2}$	—	—	—	—	1*	—	—	—
½, 3/2	0	1*	1*	1*	—	—	—	1*	1*
	$\bar{0}$	—	—	—	—	—	—	1*	—
	1	—	—	—	—	—	1*	1*	1*
	2	—	—	—	1*	—	—	1*	—
	$\bar{2}$	—	—	—	—	1*	—	1*	—
1	0	1*	1*	1*	1*	1*	—	—	1*
	$\bar{0}$	—	—	—	1*	1*	—	—	—
	1	—	—	—	—	—	1	1*	—
	2	1*	1*	1*	1*	—	—	—	—
	$\bar{2}$	1*	1*	1*	—	1*	—	—	—

$D_6, D_{3h}, D_{\infty n}, \sim_{ov}$

		$\mu=$	0	0	0	2	1	1	$\bar{0}$
		$r=$	0	0	1	0	0	1	0
		$r'=$	0	1	1	0	0	1	0
Λ	κ								
0	0		1*	1*	1*	—	—	—	—
	1		—	—	—	—	1*	—	—
	2		—	—	—	1*	—	—	—
$\frac{1}{2}, \frac{\bar{1}}{2}$	0		1*	1*	1*	—	—	1*	1*
	$\bar{0}$		—	—	—	—	—	1*	—
	1		—	—	—	—	1*	1*	1*
	2		—	—	—	1*	—	1*	—
1, 2	0		1*	1*	1*	1*	—	—	1*
	$\bar{0}$		—	—	—	1*	—	—	—
	1		—	—	—	—	1	1*	—
	2		1*	1*	1*	1	—	—	—
	3, $\bar{3}$		—	—	—	—	1*	—	—
$\frac{3}{2}$	0		1*	1*	1*	—	—	—	1*
	1		—	—	—	—	1*	1*	—
	2		—	—	—	1*	—	1	—
	3, $\bar{3}$		—	—	—	—	—	—	1*

T, T_h

	$\mu=$	0	2	1	1
	$r=$	0	0	0	1
	$r'=$	0	0	0	1
Λ	κ				
0	0	1*	—	—	—
	1	—	—	1*	—
	±2	—	1*	—	—
$\frac{1}{2}$	0	1*	—	—	1*
	1	—	—	1*	1
	±2	—	1*	—	1
1	0	1*	1*	1*	1*
	1	1*	1	1	1
	±2	1	1	1	1
$\pm\frac{3}{2}$	0	1*	1*	1*	1
	1	1*	1	1	1
	±2	1	1	1	1
±2	0	1*	1*	—	—
	1	—	—	1	1*
	±2	1	1	—	—

O, O_h, T_d

	$\mu=$	0	2	$\bar{1}$	1
	$r=$	0	0	0	0
	$r'=$	0	0	0	0
Λ	κ				
0	0	1*	—	—	—
	2	—	1*	—	—
	$\bar{1}$	—	—	1*	—
$\frac{1}{2}, \frac{\bar{1}}{2}$	0	1*	—	—	1*
	1	—	—	—	1*
	2	—	1*	—	1*
	$\bar{1}$	—	—	1*	1*
1, $\bar{1}$	0	1*	1*	1*	1*
	1	—	1	1	1*
	2, $\bar{1}$	1*	1	1	1*
	$\bar{0}$	—	1*	—	—
$\frac{3}{2}$	0	1*	1*	1*	1
	1	—	1	1	1
	2, $\bar{1}$	1*	1	1	1
	$\bar{0}$	—	1*	—	1*
2	0	1*	1*	—	—
	1	—	—	1	—
	2	1*	1	—	—
	$\bar{1}$	—	—	1	1*
	$\bar{0}$	—	1*	—	—

K

	$\mu=$	0	1	2
	$r=$	0	0	0
	$r'=$	0	0	0
Λ	κ			
0	0	1*	—	—
	2	—	—	1*
$\frac{1}{2}$	0	1*	1*	—
	1	—	1*	—
	2	—	1*	1*
1	0	1*	1*	1*
	1	—	1*	1
	2	1*	1*	1
	3	—	—	1
	$\bar{1}$	—	—	1*
$\frac{3}{2}$	0	1*	1*	1*
	1	—	1*	1
	2	1*	1	1
	3	—	1	1
	$\bar{1}$	—	1*	1*
2	0	1*	1*	1
	1, $\bar{1}$	—	1*	1
	2	1	1	1
	3	1*	1	1
$\frac{5}{2}$	0	1*	1	1
	1, $\bar{1}$	—	1	1
	2	1	1	1
	3	1*	1	1
3	0	1*	1*	1*
	1	—	1*	1
	2	1*	1	1
	3	1*	1*	1
	$\bar{1}$	—	—	1
$\bar{1}$	0	1*	—	1*
	1	—	—	1
	2	1*	1*	1
	3	—	1*	1
	$\bar{1}$	—	—	1*
$\frac{\bar{1}}{2}$	0	1*	—	—
	2	—	1*	1*
	3	—	1*	—

Table 13: Selection Rules for Phonon Raman Effect: Random Scatterers

Values of phonon symmetry κ for which the constants $c_j(\Lambda,\kappa,\Omega)$ are non zero. All non degenerate ground states $|\Lambda| = 1$ are included in the rows $\Lambda = 0$.

G	Λ \ $j=$	0	1	2
C_1				
	0	0	—	0
C_2, C_s, C_{2h}				
	0	0	—	0, 1
	$\pm\frac{1}{2}$	0	0, 1	0, 1
C_3, S_6				
	0	0	—	0, ±1
	±1	0, ±1	0, ±1	0, ±1
	$\pm\frac{1}{2}$	0	0, ±1	0, ±1
C_4, C_{4h}, S_4				
	0	0	—	0, ±1, ±2
	±1	0, 2	0, ±1	0, ±1, 2
	$\pm\frac{1}{2}, \pm\frac{3}{2}$	0	0, ±1, 2	0, ±1, 2
C_6, C_{3h}, C_{6h}				
	0	0	—	0, ±1, ±2
	±1, ±2	0, ±2	0, ±1	0, ±1, ±2, 3
	$\pm\frac{1}{2}, \pm\frac{5}{2}$	0	0, ±1, ±2	0, ±1, ±2
	$\pm\frac{3}{2}$	0	0, ±1, ±2, 3	0, ±1, ±2
D_2, D_{2h}, C_{2v}				
	0	0	—	$0, \tilde{0}, 1, \tilde{1}$
	$\frac{1}{2}$	0	$0, \tilde{0}, 1, \tilde{1}$	$0, \tilde{0}, 1, \tilde{1}$
D_3, C_{3v}, D_{3d}				
	0	0	—	0, 1
	$\frac{1}{2}$	0	$0, \tilde{0}, 1$	0, 1
	1	0, 1	1	$0, \tilde{0}, 1$
	$\pm\frac{1}{2}$	0	$0, \tilde{0}, 1$	0, 1
$D_4, C_{4v}, D_{2d}, D_{4h}$				
	0	0	—	$0, 1, 2, \tilde{2}$
	1	$0, 2, \tilde{2}$	0, 1	$0, \tilde{0}, 1, 2, \tilde{2}$
	$\frac{1}{2}, \frac{3}{2}$	0	$0, \tilde{0}, 1, 2, \tilde{2}$	$0, 1, 2, \tilde{2}$
$D_6, C_{6v}, D_{3h}, D_{6h}, C_{\infty v}, D_{\infty h}$				
	0	0	—	0, 1, 2
	1, 2	0, 2	0, 1	$0, \tilde{0}, 1, 2, 3, \tilde{3}$
	$\frac{1}{2}, \frac{5}{2}$	0	$0, \tilde{0}, 1, 2$	0, 1, 2
	$\frac{3}{2}$	0	$0, 1, 2, 3, \tilde{3}$	0, 1, 2
T, T_h				
	0	0	—	1, ±2
	±2	0, ±2	1	0, 1, ±2
	$1, \pm\frac{1}{2}$	0, 1, ±2	0, 1, ±2	0, 1, ±2
	$\frac{1}{2}$	0	0, 1, ±2	1, ±2
O, O_h, T_d				
	0	0	—	$\tilde{1}, 2$
	2	0, 2	$\tilde{1}$	$0, \tilde{0}, 1, \tilde{1}, 2$
	$1, \tilde{1}$	$0, \tilde{1}, 2$	$0, 1, \tilde{1}, 2$	$0, \tilde{0}, 1, \tilde{1}, 2$
	$\frac{1}{2}, \frac{7}{2}$	0	$0, 1, \tilde{1}, 2$	$\tilde{1}, 2$
	$\frac{3}{2}$	$0, \tilde{1}, 2$	$0, \tilde{0}, 1, \tilde{1}, 2$	$0, \tilde{0}, 1, \tilde{1}, 2$
K				
	0	0	—	2
	$\frac{1}{2}$	0	0, 1, 2	2
	1	0, 2	1, 2	$0, 1, \tilde{1}, 2, 3$
	$\frac{3}{2}$	0, 2	$0, 1, \tilde{1}, 2, 3$	$0, 1, \tilde{1}, 2, 3$
	$2, \frac{5}{2}$	0, 2, 3	$0, 1, \tilde{1}, 2, 3$	$0, 1, \tilde{1}, 2, 3$
	3	0, 2, 3	0, 1, 2, 3	$0, 1, \tilde{1}, 2, 3$
	$\tilde{1}$	0, 2	2, 3	$0, 1, \tilde{1}, 2, 3$
	$\frac{7}{2}$	0	2, 3	2

Table 14: Selection Rules for the Hyper Raman Effect

Values of the phonon symmetry κ for which the rank J terms contribute to the intensity. All non degenerate ground states $|\Lambda| = 1$ are included in the rows $\Lambda = 0$.

	Λ	J = 1	2	3
C_2, C_s	$0, \frac{1}{2}$		all κ	
C_3, C_{3i}	$0, \pm\frac{1}{2}, \pm 1$		all κ	
C_4, C_{4h}	0	0,±1	0,±1,2	0,±1,2
	$\pm\frac{1}{2}, \pm 1$		all κ	
S_4	0	±1,2	0,±1,2	0,±1,2
	$\pm\frac{1}{2}, \pm 1$		all κ	
C_6, C_{6h}	0	0,±1	0,±1,±2	0,±1,±2,3
	$\pm\frac{1}{2}$	0,±1,±2	0,±1,±2,3	0,±1,±2,3
	$\pm 1, \pm\frac{3}{2}$		all κ	
C_{3h}	0	±2,3	±1,±2,±3	0,±1,±2,3
	$\pm\frac{1}{2}$	±1,±2,3	0,±1,±2,3	0,±1,±2,3
	$\pm 1, \pm\frac{3}{2}$		all κ	
D_2, D_{2h}	0	$\tilde{0}$,1,$\tilde{1}$	0,$\tilde{0}$,1,$\tilde{1}$	0,$\tilde{0}$,1,$\tilde{1}$
	$\frac{1}{2}$		all κ	
C_{2v}	0	0,1,$\tilde{1}$	0,$\tilde{0}$,1,$\tilde{1}$	0,$\tilde{0}$,1,$\tilde{1}$
	$\frac{1}{2}$		all κ	
D_3, D_{3d}	0	$\tilde{0}$,1	0,1	0,$\tilde{0}$,1
	$\frac{1}{2}$		all κ	

C_{3v}

0	0,1	$\tilde{0}$,1	0,$\tilde{0}$,1
$\frac{1}{2}$		all κ	

D_4, D_{4h}

0	$\tilde{0}$,1	0,1,2,$\tilde{2}$	$\tilde{0}$,1,2,$\tilde{2}$
$\frac{1}{2}$		all κ	

C_{4v}

0	0,1	$\tilde{0}$,1,2,$\tilde{2}$	0,1,2,$\tilde{2}$
$\frac{1}{2}$		all κ	

D_{2d}

0	1,$\tilde{2}$	0,$\tilde{0}$,1,2	0,$\tilde{0}$,1,$\tilde{2}$
$\frac{1}{2}$		all κ	

D_6, D_{6h}

0	$\tilde{0}$,1	0,1,2	$\tilde{0}$,1,2,3,$\tilde{3}$
$\frac{1}{2},\frac{5}{2}$	0,$\tilde{0}$,1,2	0,$\tilde{0}$,1,2,3,$\tilde{3}$	0,$\tilde{0}$,1,2,3,$\tilde{3}$
$1,2,\frac{3}{2}$		all κ	

C_{6v}

0	0,1	$\tilde{0}$,1,2	0,1,2,3,$\tilde{3}$
$\frac{1}{2},\frac{5}{2}$	0,$\tilde{0}$,1,2	0,$\tilde{0}$,1,2,3,$\tilde{3}$	0,$\tilde{0}$,1,2,3,$\tilde{3}$
$1,2,\frac{3}{2}$		all κ	

D_{3h}

0	2,$\tilde{3}$	1,2,3	0,$\tilde{0}$,1,2,$\tilde{3}$
$\frac{1}{2},\frac{5}{2}$	1,2,3,$\tilde{3}$	0,$\tilde{0}$,1,2,3,$\tilde{3}$	0,$\tilde{0}$,1,2,3,$\tilde{3}$
$1,2,\frac{3}{2}$		all κ	

T, T_h

0	1	1,±2	0,1
±2	1	0,1,±2	0,1,±2
$1,\frac{1}{2},\pm\frac{3}{2}$		all κ	

O, O_h

0	1	2,$\tilde{1}$	1,$\tilde{1}$,$\tilde{0}$
$\frac{1}{2},\tilde{\frac{1}{2}}$	0,1,$\tilde{1}$,2	$\tilde{0}$,1,$\tilde{1}$,2	0,$\tilde{0}$,1,$\tilde{1}$,2
2	1,$\tilde{1}$	0,$\tilde{0}$,1,$\tilde{1}$,2	0,$\tilde{0}$,1,$\tilde{1}$,2
$1,\tilde{1},\frac{3}{2}$		all κ	

T_d

0	$\tilde{1}$	$1,2$	$0,1,\tilde{1}$
$\frac{1}{2},\tilde{\frac{1}{2}}$	$\tilde{0},1,\tilde{1},2$	$0,1,\tilde{1},2$	$0,\tilde{0},1,\tilde{1},2$
2	$1,\tilde{1}$	$0,\tilde{0},1,\tilde{1},2$	$0,\tilde{0},1,\tilde{1},2$
$1,\tilde{1},\frac{3}{2}$		all κ	

K

0	1	2	$3,\tilde{1}$
$\frac{1}{2}$	$0,1,2$	$1,2,3,\tilde{1}$	$2,3,\tilde{1}$
1	$0,1,2,3,\tilde{1}$	$0,1,2,3,\tilde{1}$	$1,2,3,\tilde{1}$
$\tilde{\frac{1}{2}}$	$1,2,3$	$1,2,3,\tilde{1}$	$0,1,2,3,\tilde{1}$
$\tilde{1}$	$1,2,3,\tilde{1}$	$0,1,2,3,\tilde{1}$	$0,1,2,3,\tilde{1}$
$2,3,\frac{3}{2},\frac{5}{2}$		all κ	

Table 15: Selection Rules for Magnetic Circular Dichroism

The form of the non zero geometrical factors contributing to the M.C.D. spectrum (equation 5.12). Normalisation factors are omitted. $(e_\rho e_\sigma)_- \equiv e_\rho e_\sigma^* - e_\sigma e_\rho^*$

R_3, K, O, O_h, Td	$\underline{B}\cdot(\underline{e} \times \underline{e}^*)$
$D_6, D_{6h}, C_{6v}, C_{3h}$ $D_4, D_{4h}, C_{4v}, D_{2d}$ D_3, D_{3d}, C_{3v}	$B_z(e_x e_y)_-$ $B_x(e_y e_z)_- + B_y(e_x e_z)_-$
D_2, D_{2h}, C_{2v}	$B_x(e_y e_z)_-$ $B_y(e_z e_x)_-$ $B_z(e_x e_y)_-$
C_6, C_{6h}, C_{3h} C_4, C_{4h}, S_4 C_3, C_{3i}	$B_z(e_x e_y)_-$ $B_x(e_y e_z)_- + B_y(e_z e_x)_-$ $B_x(e_z e_x)_- - B_y(e_y e_z)_-$
C_2, C_{2h}, C_s	$B_z(e_x e_y)_-$ $B_x(e_z e_x)_-$ $B_x(e_y e_z)_-$ $B_y(e_z e_x)_-$ $B_y(e_y e_z)_-$

Table 16: Selection Rules for Electric Circular Dichroism

The form of the non zero geometrical factors contributing to the E.C.D. spectrum (equation 5.21). Normalisation factors are omitted. $(e_\rho\ e_\sigma)_+ \equiv e_\rho e^*_\sigma + e_\sigma e^*_\rho$.

R_3, K, O, O_h, Td	forbidden
T, T_h	$E_z(e_x e_y)_+ + E_y(e_z e_x)_+ + E_x(e_z e_y)_+$
$D_6, D_{6h}, C_{6v}, C_{3h}$ $D_4, D_{4h}, C_{4v}, D_{2d}$	$E_x(e_y e_z)_+ + E_y(e_z e_x)_+$
D_3, D_{3d}, C_{3v}	$E_x(e_x e_y)_+ + E_y(e_x e^*_x - e_y e^*_y)$ $E_x(e_y e_z)_+ - E_y(e_z e_x)_+$
D_2, D_{2h}, C_{2v}	$E_z(e_x e_y)_+$ $E_y(e_z e_x)_+$ $E_x(e_y e_z)_+$
C_6, C_{6h}, C_{3h} C_4, C_{4h}, S_4	$E_z(e_x e^*_x + e_y e^*_y + e_z e^*_z)$ $E_z(e_x e^*_x + e_y e^*_y - 2e_z e^*_z)$ $E_x(e_y e_z)_+ - E_y(e_z e^*_x)$ $E_x(e_z e^*_x)_* + E_y(e_y e^*_z)$
C_3, C_{3i}	$E_z(e_x e^*_x + e_y e^*_y + e_z e^*_z)$ $E_z(e_x e^*_x + e_y e^*_y - 2e_z e^*_z)$ $E_x(e_x e_y)_+ + E_y(e_x e^*_x - e_y e^*_y)$ $E_x(e_x e^*_x - e_y e^*_y) - E_y(e_x e_y)_+$ $E_y(e_z e_x)_+ - E_x(e_y e_z)_+$ $E_x(e_z e_x)_+ + E_y(e_y e_z)_+$
$C_2, C_{2h}, (C_s)$	$E_z(e_x e^*_x + e_y e^*_y + e_z e^*_z)$ $E_z(e_x e^*_x + e_y e^*_y - 2e_z e^*_z)$ ← $y \leftrightarrow z$ $E_z(e_x e^*_x - e_y e^*_y)$ ← for C_s $E_x(e_y e_z)_+$; $E_x(e_z e_x)_+$ $E_y(e_z e_x)_+$; $E_y(e_y e_z)_+$ $E_z(e_x e_y)_+$

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Phonon Raman spectroscopy in systems with electronic degeneracy

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Abstract. The theory of the vibrational or phonon Raman spectrum of molecules or solids in the non-resonant regime is formulated for systems with electronic degeneracy. A selection rule is established, extending that of Child; previous disagreement on this selection rule is reviewed. Symmetric and antisymmetric parts of the scattering amplitude are proved to combine incoherently, as observed by Kiel and co-workers. Tables of Raman scattering contributions in non-degenerate systems, for oriented scatterers by Loudon and for orientationally averaged scatterers by McClain, are generalised to systems with electronic degeneracy. This should greatly facilitate the assignment of spectral lines in systems with Jahn–Teller or Kramers degenerate ground states, and constitutes the first step in determining a strategy for the economical extraction of the information available through Raman spectroscopy. An alternative recoupling is considered following work in quantum beat spectroscopy. This will prove advantageous when only linear polarisation is used, or when particular intermediate state symmetries are important.

1. Introduction

It is well known from the work of Placzek in 1934 (Placzek 1962) that the phonon Raman scattering amplitude is symmetrical in the polarisation indices for incoming and outgoing photons, provided that the ground electronic state is non-degenerate, and that an approximation to the energy denominators, appropriate to the non-resonant limit, is valid. When either of these conditions is disobeyed, an antisymmetric term is to be anticipated in general. For given symmetry types of the electronic state and of the phonon, it may be possible to prove that either the symmetric or the antisymmetric part of the scattering amplitude vanishes. Such selection rules were derived by Child and Longuet-Higgins (1962) for the case of Jahn–Teller active systems, and by Child (1963) for the case of Kramers (time-reversal) degeneracy. However, later authors (Mulazzi and Terzi 1976, 1979) have independently offered an inequivalent selection rule, and one of the consequences of Child's (1963) selection rule has been contradicted by Parameswaram *et al* (1977).

We generalise the method of Loudon (1964) to systems possessing time reversal or orbital degeneracy. Our selection rule is consistent with those of Child (1963) and Child and Longuet-Higgins (1962), but is somewhat stronger. This permits a proof that the symmetric and antisymmetric parts of the scattering amplitude never interfere, i.e. only combine incoherently in the final intensity, provided the non-resonant limit is valid. This is well known in the case of orientationally averaged scatterers, where it holds even

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outside the non-resonant limit. However, for oriented scatterers, the lack of coherence between symmetric and antisymmetric terms is not obvious, even on the selection rule of Child (1963). Our analysis thus explains the unexpected null result of Kiel *et al* (1969), who searched for interference between the symmetric and antisymmetric scattering amplitudes in the phonon Raman spectrum of $CeCl_3$.

The symmetries of the Raman scattering amplitude for the case of non-degenerate electronic states have been tabulated in several places (e.g. Loudon 1964, McClain 1971, Cummins and Schoen 1972). Little progress has been made in generalising to systems with electronic degeneracy, and that progress has been mostly in the closely related theory of two-photon spectroscopy (Worlock 1972). In § 3 we tabulate the symmetries of the Raman scattering intensity for all choices of site group, electron and phonon symmetry, and all values of the polarisation vectors. The symmetries of the scattering intensity depend critically on the use of the correct selection rule. Given either of the electronic or vibrational symmetries, the other may be deduced usually without ambiguity from the observed symmetry of the Raman scattering intensity and the aid of these tables. We hope that this will assist the assignment of spectral lines in systems possessing electronic degeneracy.

Connections with other workers are described. The group theoretical methods of §§ 4 and 5 were used initially for the case of SO_3 symmetry (orientationally averaged scatterers) by Fano and Racah (1959) and independently by Yuratich and Hanna (1976) (see also Omont 1977, Chen and Yueng 1979); this eliminates the averaging of products of direction cosines performed in many standard presentations and in recent work (Sushchinskii 1972, Andrews and Thirunamachandran 1978). We extend this to point groups (oriented scatterers). Similar work was pioneered by Inoue and Toyozawa (1965); for more recent papers see Denisov and Makarov (1972, 1973) and Doni *et al* (1974). However, many of the assumptions made in these works, particularly that of invariant initial electronic states, are not generally applicable. Diagram techniques have been used before in this connection for SO_3 symmetry by Yuratich and Hanna (1976), also Cotter and Hanna (1976). Axe (1964) has used tensorial techniques when discussing approximations of the sum over intermediate states. Our approach (Appendix 1, §§ 4 and 5) is based on earlier diagrammatic formulations of the Raman spectrum (McKenzie and Stedman 1978, see also Zaidi 1979, Saunders and Young 1980) and of group theory (Stedman 1975, 1976) including time-reversal symmetry (Stedman and Butler 1980). As such, the work is based on a third-order perturbation theoretic approach rather than the adiabatic formulation used by Placzek (1962) and Child (1963); an interesting comparison of these methods is given by Johnson and Peticolas (1976). The recoupling techniques of group theory help to establish the connection between the approaches of Placzek (1962) and of McClain (1971), and of the rather different approach of workers in resonance fluorescence (Dodd and Series 1978) (§ 5). The alternative coupling suggested by that approach is of value when linear polarisation is used, or when particular intermediate state symmetries are of importance.

2. Raman scattering from oriented centres; selection rules

2.1. Introduction

We consider first the case of oriented scatterers, e.g. host or substitutional impurity ions in a crystal. It is generally accepted (Loudon 1964) that the electronic levels of these

ions mediate the coupling between photons and phonons that results in Stokes and anti-Stokes phonon lines, and that third-order perturbation theoretic calculations of the scattering are adequate. This implies that we shall consider an electron–radiation interaction which is linear in photon operators, as in the dipole approximation. We shall consider either electric dipole or magnetic dipole couplings, but ignore interference between these (e.g. optical activity), which will be discussed separately.

Consider a particular feature in the first-order phonon Raman spectrum, corresponding to a set of phonon modes κ with energy $\omega_\kappa(\hbar \equiv 1)$; the corresponding Latin label k will enumerate partners (equi-energetic modes) in this set. Electronic levels of the ion will be labelled by capital Greek letters, and the states within each energy level by the corresponding lower case Latin letter; in particular, we label the ground states by $\{\Lambda l, l = 1, 2, \ldots\}$. The incoming (outgoing) light has frequency ω_{in} (ω_{out}) and polarisation $\boldsymbol{e}(\boldsymbol{e}')$; we write the set of frequencies $\Omega = (\omega_{\text{in}}, \omega_{\text{out}}, \omega_\kappa)$. The intensity of the phonon Raman feature is proportional to (e.g. Stein *et al* 1977)

$$I_{ee'}(\Omega) = \sum_{kll'} |\sum_{\rho\rho'} e_\rho R^{kll'}_{\rho\rho'}(\Omega) e'_{\rho'}|^2 \tag{1}$$

where the scattering amplitude is given by

$$R^{kll'}_{\rho\rho'}(\Omega) = \sum_{AaBb} \frac{\langle \Lambda\bar{l}|M_\rho|Bb\rangle\langle Bb|M_{\rho'}|Aa\rangle\langle Aa|V_k|\Lambda l'\rangle}{(\omega_B - \omega_\Lambda + \omega_{\text{in}})(\omega_A - \omega_\Lambda + \omega_K)} + 5 \text{ terms} \tag{2}$$

and where the other five terms correspond to alternative orderings of the three interactions, with corresponding adjustments of the denominators. M_ρ and $M_{\rho'}$ are the interaction operators for coupling to incoming and outgoing photons, and V_k the interaction associated with creation of a phonon in lattice mode κk. For simplicity later, we have added a bar to a ground state label ($l \rightarrow \bar{l}$) thus re-defining this state as its time-reversal conjugate, which is degenerate with it in the absence of a magnetic field.

Earlier work has usually been limited to considering singlet levels only ($|\Lambda| = 1$, $l = l' = 0$). Loudon (1963) showed that in this case

$$R^k_{\rho\rho'}(\Omega) = R^k_{\rho'\rho}(\Omega') \tag{3}$$

where $\Omega' = (\omega_{\text{out}}, \omega_{\text{in}}, -\omega_\kappa)$. In the non-resonant limit, and since $\omega_\kappa \ll \omega_{\text{in}}$, it is reasonable to assume that $\Omega' = \Omega$ in evaluating the denominators, so that $R^k_{\rho\rho'}(\Omega) = R^k_{\rho'\rho}(\Omega)$, i.e. the phonon Raman scattering amplitude is symmetric in the non-resonant case for singlet ground state levels.

It is straightforward to generalise this result. Using the hermiticity and time-reversal symmetry of each interaction (e.g. Abragam and Bleaney 1970, Stedman and Butler 1980)

$$R^{kll'}_{\rho\rho'}(\Omega) = \tau_\Lambda R^{kl'l}_{\rho'\rho}(\Omega') \doteq \tau_\Lambda R^{kl'l}_{\rho'\rho}(\Omega) \qquad (\text{NR}). \tag{4}$$

The phase $\tau_\Lambda = \pm 1$ as the electronic state corresponds to an even or odd number of electrons. As in the proof of Loudon (1963) we take the interactions to be time-reversal even, and pair the terms in equation (2) to achieve equation (4). The label NR identifies equations which are only true in a non-resonant approximation.

2.2. *Group-theoretic definitions*

The various electronic and lattice states may be classified using the irreducible representations (irreps) of a point group G (table 1). In this work we take this group to be the

Table 1. Alternative notation for irrep labels in point groups. We list the notations of Butler (1981), Koster *et al* (1963) and also of Mulliken (for at least the true irreps distinguishing groups within a table where necessary). Butler's notation is more systematic ($0 \equiv$ identity irrep; $\frac{1}{2} \sim |j = m = \frac{1}{2}\rangle$; $-\lambda \equiv \lambda^*$; $\lambda \otimes \bar{O} \sim \tilde{\lambda}$, etc.) and is used elsewhere in this paper. For groups containing the inversion, read Γ^+ for Γ and X_g for X in the Koster *et al* and Mulliken notations respectively.

C_2, C_{2h}, C_s
(2, 2/m, m)

	0	$\frac{1}{2}$	$-\frac{1}{2}$	1
	Γ_1	Γ_3	Γ_4	Γ_2
C_2:	A			B
C_s:	A′			A″

C_3, C_{3i}
$(3, \bar{3})$

0	$\frac{1}{2}$	$-\frac{1}{2}$	1	-1	$\frac{3}{2}$
Γ_1	Γ_4	Γ_5	Γ_2	Γ_3	Γ_6
A			E		

C_4, C_{4h}, S_4
$(4, 4/m, \bar{4})$

0	$\frac{1}{2}$	$-\frac{1}{2}$	1	-1	$\frac{3}{2}$	$-\frac{3}{2}$	2
Γ_1	Γ_5	Γ_6	Γ_3	Γ_4	Γ_8	Γ_7	Γ_2
A			E				B

C_6, C_{3h}, C_{6h}
$(6, \bar{6}, 6/m)$

	0	$\frac{1}{2}$	$-\frac{1}{2}$	1	-1	$\frac{3}{2}$	$-\frac{3}{2}$	2	-2	$\frac{5}{2}$	$-\frac{5}{2}$	3
	Γ_1	Γ_7	Γ_8	Γ_5	Γ_6	Γ_{12}	Γ_{11}	Γ_3	Γ_2	Γ_{10}	Γ_9	Γ_4
C_6:	A			E_1				E_2				B
C_{3h}:	A′			E″				E′				A″

D_2, C_{2v}, D_{2h}
(222, mm2, mmm)

	0	$\frac{1}{2}$	$\tilde{0}$	1	$\tilde{1}$
	Γ_1	Γ_5	Γ_3	Γ_2	Γ_4
D_2:	A_1	E′	B_1	B_2	B_3
C_{2v}:	A_1		A_2	B_1	B_2

Table 1—continued

D_3, C_{3v}, D_{3d},
(32, 3m, $\bar{3}$m

0	$\frac{1}{2}$	$\tilde{0}$	1	$\frac{3}{2}$	$-\frac{1}{2}$
Γ_1	Γ_4	Γ_2	Γ_3	Γ_5	Γ_6
A_1	E′	A_2	E	E″	

D_4, D_{4h}, C_{4v}, D_{2d}
(422, 4/mmm, 4mm, $\bar{4}$2m)

0	$\frac{1}{2}$	$\tilde{0}$	1	$\frac{3}{2}$	2	$\tilde{2}$
Γ_1	Γ_6	Γ_2	Γ_5	Γ_7	Γ_3	Γ_4
A_1	E′	A_2	E	E″	B_1	B_2

D_6, C_{6v}, D_{3h}, D_{6h}
(622, 6mm, $\bar{6}$m2, 6/mmm)

	0	$\frac{1}{2}$	$\tilde{0}$	1	$\frac{3}{2}$	2	$\frac{5}{2}$	3	$\tilde{3}$
	Γ_1	Γ_7	Γ_2	Γ_5	Γ_9	Γ_6	Γ_8	Γ_3	Γ_4
D_6:	A_1	E′	A_2	E_1	E‴	E_2	E″	B_1	B_2
D_{3h}:	A_1'		A_2'	E″		E′		A_1''	A_2''
C_{6v}:	A_1		A_2	E_1		E_2		B_2	B_1

T, T_h
(23, m3)

0	$\frac{1}{2}$	1	$\frac{3}{2}$	$-\frac{1}{2}$	2	−2
Γ_1	Γ_5	Γ_4	Γ_6	Γ_7	Γ_2	Γ_3
A_1	E′	T	E″	E‴	E	

O, O_h, T_d
(432, m3m, $\bar{4}$3m)

0	$\frac{1}{2}$	1	$\frac{3}{2}$	2	$\tilde{1}$	$\tilde{\frac{1}{2}}$	$\tilde{0}$
Γ_1	Γ_6	Γ_4	Γ_8	Γ_3	Γ_5	Γ_7	Γ_2
A_1	E′	T_1	U′	E	T_2	E″	A_2

K

0	$\frac{1}{2}$	1	$\frac{3}{2}$	2	$\frac{5}{2}$	3	$\tilde{1}$	$\tilde{\frac{1}{2}}$
A_1	E′	T_1	U′	V	W′	U	T_2	E″

symmetry group of the electronic system (substitutional impurity or host ion) mediating the scattering process. (In a crystal, as opposed to a molecule, it must be recognised that the appropriate point group for a description of the phonons is the $k = 0$ factor group of the space group (Birman and Berenson 1974), so that a lattice mode may activate more than one of the phonon mode irreps listed in this paper.) Lower case Greek letters will denote irrep labels, and the dimensions will be indicated by carets (dimension of $\kappa = |\kappa| = \hat{\kappa} = (\hat{\kappa})^2 = (\check{\kappa})^{-2}$) . The electronic states Λl, $\Lambda l'$ and their time-reversal conjugates $\Lambda\bar{l}$, $\Lambda\bar{l}'$, if distinct, all form partners of a representation Λ of G. We have used a capital letter, since while Λ is an irreducible co-representation of the space–time group $G + \theta G$ (θ representing time reversal), Λ may be reducible with respect to the point group: $\Lambda = \Sigma_{a\lambda} a\lambda$ where λ is a corresponding irrep and a is a branching multiplicity label. If l_0 is a component of λ we write the basis transformation for the reduction $\Lambda \downarrow \lambda$ as $\langle \Lambda l | a\lambda l_0 \rangle$. Likewise the $j = 1^-$ irrep of O_3 reduces to an irrep (or irreps) π of G. This branching may be used to define the irreducible parts of the photon interaction:

$$M_\rho = \sum_{\pi p} \langle a\pi p | 1\rho \rangle M_p^{\pi a}. \tag{5}$$

The multiplicity label a, corresponding to repetitions of irrep π in the branching of $j = 1^-$, is non-trivial only for $G = C_2, C_{1h}, S_2$. We now find it useful to define a generalisation of the $3jm$ symbol of point group theory, given by combining the standard $3jm$ symbol with the basis transformations to a reducible basis. In particular we define

$$\begin{pmatrix} \Lambda & \Lambda & \nu^* \\ l & l' & n^* \end{pmatrix}^r = \sum_{l_0 l'_0} \langle a\lambda l_0 | \Lambda l \rangle \langle a'\lambda' l'_0 | \Lambda l' \rangle \begin{pmatrix} \lambda & \lambda' & \nu^* \\ l_0 & l'_0 & n^* \end{pmatrix}^{r'} \tag{6}$$

$$\begin{pmatrix} 1 & 1 & \mu^* \\ \rho & \rho' & m^* \end{pmatrix}^r = \sum_{pp'} \langle a\pi p | 1\rho \rangle \langle a'\pi' p' | 1\rho' \rangle \begin{pmatrix} \pi & \pi' & \mu^* \\ p & p' & m^* \end{pmatrix}^{r'}. \tag{7}$$

We call the left sides reducible $3jm$ symbols. They have similar unitarity properties to those of the standard $3jm$ symbols, since the basis transformations are unitary. Again, as with standard $3jm$ symbols with two equal representations, their interchange permutation symmetries correspond to the symmetry of the appropriate Kronecker products. That is to say, under exchange of the first two columns in equation (6), this reducible $3jm$ symbol changes by a phase $\{\Lambda\Lambda\nu^* r\}$ which equals ± 1 as the rth occurrence of ν in $\Lambda \otimes \Lambda$ occurs in the symmetric or antisymmetric part respectively. The product multiplicity labels r, r' are unrelated between equations (6) and (7), and in each case r is an abbreviation for (a, a', r'). Note that quasi-ambivalence does not generalise; $r \neq r^*$ since $a \neq a^*$ in general. The Derome–Sharp lemma becomes, for example,

$$\begin{pmatrix} 1 & 1 & \mu^* \\ \rho & \rho' & m^* \end{pmatrix}^r = \begin{pmatrix} 1 \\ \rho \end{pmatrix}^* \begin{pmatrix} 1 \\ \rho' \end{pmatrix}^* \begin{pmatrix} \mu^* \\ m^* \end{pmatrix}^* A^*_{rr^*} \left[\begin{pmatrix} 1 & 1 & \mu \\ \rho^* & \rho'^* & m \end{pmatrix}^{r^*} \right]^*$$

(A_{rr^*}) being a unitary matrix composed of 1's and 0's. We note that $1 \otimes 1$ can only branch into orthogonal (where $\{\mu\} \equiv 1$) or true complex irreps, and $\{\mu\}$ is invariably chosen to be unity in the latter case (Stedman and Butler 1980). We shall use this in the following sections. In particular, we define our choice of reducible $3jm$ factors in Appendix 2, and determine to what extent quasi-ambivalence (in the sense $\{j\} = \{\mu\}$) limits the form of the matrix $(A_{rr'})$. We find that $A_{rr'} = \varepsilon_r^\mu \delta_{rr'}$, with $\varepsilon_r^\mu = \pm 1$.

2.3. Group-theoretic reduction; selection rules

With these preliminaries, we are in a position to couple the operators within the matrix elements of equation (2) and apply the Wigner–Eckart theorem for the point group to the combination. The intermediate state projections and the denominators are invariant under point group operations, and do not affect the analysis. This yields the equation

$$R^{kll'}_{\rho\rho'}(\Omega) = \sum_{\mu\nu r} A^{kll'}_{\rho\rho'}(\mu, \nu, r) f_{\mu\nu r}(\Lambda, \kappa, \Omega) \tag{8}$$

where

$$A^{kll'}_{\rho\rho'}(\mu, \nu, r) \equiv \sum_{mn} \hat{\mu}\hat{\nu} \begin{pmatrix} \Lambda & \Lambda & \nu^* \\ l & l' & n^* \end{pmatrix}^{r_1} \begin{pmatrix} 1 & 1 & \mu^* \\ \rho & \rho' & m^* \end{pmatrix}^{r_2} \begin{pmatrix} \mu & \kappa & \nu \\ m & k & n \end{pmatrix}^{r_3} \begin{pmatrix} \mu \\ m \end{pmatrix} \begin{pmatrix} \nu \\ n \end{pmatrix} \tag{9}$$

$$f_{\mu\nu r}(\Lambda, \kappa, \Omega) = \sum_{kll'\rho\rho'} [A^{kll'}_{\rho\rho'}(\mu, \nu, r)]^* R^{kll'}_{\rho\rho'}(\Omega) \tag{10}$$

$$\propto \langle \Lambda \| O^{\nu} \| \Lambda \rangle_{r_1} \langle 1 \| O^{\mu} \| 1 \rangle_{r_2} \langle r_2^* \mu^* \| O^{\kappa} \| r_1 \nu \rangle_{r_3} \tag{11}$$

and $r = (r_1, r_2, r_3)$. Each term in equation (2) gives a result of this form; any recoupling necessary ($6j$ symbols) may be incorporated in the constants $f_{\mu\nu r}(\Lambda, \kappa, \Omega)$ together with the reduced matrix elements given explicitly above, the summations over excited states etc.

For a non-degenerate ground state $\Lambda(|\Lambda| = 1)$ equation (8) reduces to

$$h_{\rho\rho' k}(\Omega) = \sum_{r} \begin{pmatrix} 1 & 1 & \kappa \\ \rho & \rho' & k \end{pmatrix}^{r} f_{k^* 0 r}(\Lambda, \Omega) \tag{12}$$

which are the tensor elements $(a, b, \ldots)$ of the tables of Loudon (1964), McClain (1971) etc. On the face of it, equation (12) implies a summation over symmetric and antisymmetric occurrences of κ in $1 \otimes 1$. However, this is corrected by the selection rule that we shall prove. In this sense equation (1) of McClain (1971) is incorrect; the symmetric and antisymmetric parts of his tabulation need separate treatment.

Equation (9) implies the selection rules

$$(\mu)_{r_2} \in 1 \otimes 1 \qquad (\nu)_{r_1} \in \Lambda \otimes \Lambda \qquad (\mu^*)_{r_3} \in \kappa \otimes \nu. \tag{13}$$

The permutation symmetries discussed with equations (6), (7) then give in equation (9)

$$A^{kll'}_{\rho\rho'}(\mu, \nu, r) = \{1\ 1 \mu^* r_2\} \{\Lambda\Lambda \nu^* r_1\} A^{kl'l}_{\rho'\rho}(\mu, \nu, r). \tag{14}$$

Combining equations (4), (10) and (14), we find that in the non-resonant case, $f_{\mu\nu r}(\Lambda, \kappa, \Omega)$ is non-zero only if

$$\tau_{\Lambda}\{1\ 1 \mu r_2\} \{\Lambda\Lambda \nu r_1\} = 1 \qquad \text{(NR)}. \tag{15}$$

Hence equation (13) becomes

$$(\nu)_{r_1} \in [\Lambda \otimes \Lambda]_{\eta\tau_{\Lambda}} \qquad (\mu)_{r_2} \in [1 \otimes 1]_{\eta} \qquad (\mu^*)_{r_3} \in \kappa \otimes \nu \tag{16}$$

with $\eta = \pm 1$ corresponding to symmetric and antisymmetric scattering. For example, for $|\Lambda| = 1$ equation (16) becomes $\kappa \in [1 \times 1]_+$, i.e. symmetric scattering only.

The selection rule of equation (16) is stronger than (but consistent with) that of Child (1963), because of the inclusion of multiplicity labels r. The strong form of this selection rule is essential for proving later results.

Mulazzi and Terzi (1976, 1979) give a selection rule in which the phase τ_Λ is absent. There seem to be other problems with these works. For example, Mulazzi and Terzi (1979) seem to put $l = l'$ in equation (1), and claim that when $G = O_h$, for example, only phonons with $\kappa = \Gamma_1, \Gamma_3, \Gamma_5$ are Raman active when $\Lambda = \Gamma_3$. We find that all phonon symmetry types are allowed, for this choice of G and Λ. Parameswaram *et al* (1977) explicitly disagree with Child (1963); we discuss this discrepancy in § 4.

Equation (1), coupled with equation (4), gives the reciprocity condition

$$I_{ee'}(\Omega) = I_{e'e}(\Omega) \qquad \text{(NR)}. \tag{17}$$

This seems to have escaped the notice of earlier workers: the Raman scattering intensity is symmetric in the non-resonant case, even though the Raman scattering amplitude may contain an antisymmetric part. Thus Kiel *et al* (1969), who searched for an antisymmetric component of the intensity in the phonon Raman spectrum of $CeCl_3$, were bound to find a null result, even although (as they correctly believed) the amplitude had both a symmetric and antisymmetric component. Equation (17) implies that these components do not interfere. We shall now prove this explicitly.

Combining equations (1), (8), (9) and using the unitarity of the $3jm$ symbols, we may prove that

$$I_{ee'}(\Omega) = \sum_{\mu\nu m r_1 r_3} \left| \sum_r [ee']^{\mu r}_m f_{\mu\nu r}(\Lambda, \kappa, \Omega) \right|^2. \tag{18}$$

This may also be expanded in the form

$$I_{ee'}(\Omega) = \sum_{\mu r r'} F_{\mu r r'}(e, e')\, c_{\mu r r'}(\Lambda, \kappa, \Omega) \tag{19}$$

where the geometrical and physical factors are

$$F_{\mu r r'}(e, e') = \sum_m \hat{\mu} [ee']^{\mu r}_m ([ee']^{\mu r'}_m)^* \tag{20}$$

$$c_{\mu r r'}(\Lambda, \kappa, \Omega) = \sum_{\nu r_1 r_3} \hat{\mu} \hat{r} f_{\mu\nu r}(\Lambda, \kappa, \Omega) f^*_{\mu\nu r'}(\Lambda, \kappa, \Omega). \tag{21}$$

In these equations $\boldsymbol{r} = (r_1, r, r_3)$, $\boldsymbol{r}' = (r_1, r', r_3)$ and

$$[ee']^{\mu r}_m \equiv \sum_{\rho\rho'} \begin{pmatrix} \mu \\ m \end{pmatrix} \begin{pmatrix} 1 & 1 & \mu^* \\ \rho & \rho' & m^* \end{pmatrix}^r e_\rho e'_{\rho'}. \tag{22}$$

Equations (18), (19) give a generalisation of the results of Inoue and Toyozawa (1965) and subsequent authors. A different method of proof will be sketched in § 5.

The selection rule (15), for the non-vanishing of the constant $f_{\mu\nu r}(\Lambda, \kappa, \Omega)$, must hold for each of these constants in equation (21) if $c_{\mu r r'}(\Lambda, \kappa, \Omega)$ is not to vanish. Each application of equation (15) contains the same phase $\tau_\Lambda\{\Lambda\Lambda\nu r_1\}$, whose square is unity. Therefore the remaining phases must also be equal, i.e.

$$\{1\ 1 \mu r\}\{1\ 1 \mu r'\} = 1 \qquad \text{(NR)}. \tag{23}$$

(Alternatively, one may combine the symmetry of equation (17) with equations (20) and (22).) This is equivalent to saying that the symmetric and antisymmetric components of the amplitude never interfere.

A very simple justification of equation (17) is given by the principle of detailed balance, or microscopic reversibility. In the non-resonant regime, the phonon has negligible energy and may as well be absorbed as emitted; the time-reversed state is

equivalent to the original. Kiel *et al* (1969) in fact state the principle of detailed balance in their equation (5), but failed to note the above application, presumably because the non-resonant approximation if taken too literally would collapse the Stokes and anti-Stokes phonon spectrum onto the laser line.

Finally, time-reversal symmetry constrains the reduced matrix elements given in equation (11) (Stedman and Butler 1980) in such a manner that

$$f_{\mu\nu r}(\Lambda, \kappa, \Omega) = A_{rr^*} f^*_{\mu^*\nu^* r^*}(\Lambda, \kappa, \Omega). \tag{24}$$

It follows that the amplitude $R^{kll'}_{\rho\rho'}(\Omega)$ is self-conjugate (satisfies a generalised Derome–Sharp lemma, Appendix 1). This gives an alternative proof of equation (4).

3. Raman scattering from oriented centres; polarisation dependence

For oriented centres, the most economical description of the Raman scattering spectrum is given in equation (19) as a sum of products of geometrical factors $F_{\mu rr'}(e, e')$ (which epitomise the various polarisation dependences appropriate to any point group G and coupling symmetry μ) and physical constants $c_{\mu rr'}(\Lambda, \kappa, \Omega)$ (whose magnitudes reflect the details of the physical interactions responsible for the scattering spectrum). From now on we suppress the symbols Λ, κ, Ω in $c_{\mu rr'}$.

The maximum information that can be obtained in a Raman scattering experiment from various experimental arrangements, i.e. crystal orientation, scattering geometry, polariser and analyser settings, is the set of 'reduced' spectra defined by the constants $\{c_{\mu rr'}\}$ as functions of frequency Ω. Where phonon lines overlap, it may be necessary to combine the results from several experimental arrangements in order to determine uniquely the contribution to the spectrum from some particular value of μ or κ (e.g. Fröhlich *et al* 1970). The strategy of such reductions has not been developed for a general case; we consider this problem elsewhere.

A simpler but related problem is that of assignment of well separated phonon lines, i.e. determination of the appropriate irrep labels κ and/or Λ for any spectral feature. Because of the selection rule of equation (15), the number of different constants $c_{\mu rr'}$ which may be combined in the intensity is constrained by the choice of electronic symmetry κ. The resulting symmetries of the intensity $I_{ee'}(\Omega)$ may then be sufficiently characteristic for unambiguous assignments to be made from a very few measurements.

To this end, we generalise the familiar tables for the symmetries of the scattering amplitude in non-degenerate systems, and construct tables of the symmetries of the scattering intensity in degenerate systems.

It is helpful to introduce at this stage some new nomenclature. We define a vector $\tilde{e}$, conjugate to the polarisation vector e, by

$$\tilde{e}_\rho = \begin{pmatrix} 1 \\ \rho \end{pmatrix} (e_{\rho^*})^*. \tag{25}$$

where $\binom{1}{\rho}$ is the $2jm$ symbol for the irrep $j = 1$ of SO_3 in the basis $\{\rho\}$. In a cartesian basis ($\rho = x, y, z$) the $2jm$ symbol is trivial and $\rho^* = \rho$ (equation (46)), so that $\tilde{e} = e^*$. However, we include the $2jm$ symbol in all our formulation so that a reader who prefers a spherical tensor basis can adapt our results, e.g., for circular polarisation studies. We use the contrastandard transformation of Fano and Racah (1959), namely $\rho = 1 \equiv (y - ix)/\sqrt{2}$, $\rho = 0 \equiv iz$, $\rho = -1 \equiv (y + ix)/\sqrt{2}$; the unconventional imaginary factor ensures that the transformed Wigner $3j$ symbol (equation (46)) is real. The

definition of equation (25) is basis-independent, and satisfies the conjugacy property $\tilde{\tilde{e}} = e$; the self-conjugate case $\tilde{e} = e$ always corresponds to that of linearly polarised light. Normalisation gives $e \cdot e^* = e_\rho \tilde{e}_{\rho^*} (^1_\rho)^* = 1$.

In this notation, equation (20) becomes

$$F_{\mu rr'}(e, e') = \sum_{\rho\rho'\sigma\sigma'} \hat{\mu} \varepsilon^\mu_r \begin{pmatrix} 1 & 1 & \mu^* \\ \rho & \rho' & m^* \end{pmatrix}^r \begin{pmatrix} 1 & 1 & \mu \\ \sigma & \sigma' & m \end{pmatrix}^{r'} \begin{pmatrix} \mu \\ m \end{pmatrix} e_\rho e'_{\rho'} \tilde{e}_\sigma \tilde{e}'_{\sigma'} \tag{26}$$

so that

$$F_{\mu rr'}(e, e') = F^*_{\mu r' r}(e, e') \tag{27}$$

$$= \varepsilon^\mu_r \varepsilon^\mu_{r'} F_{\mu^* r' r}(\tilde{e}, \tilde{e}'). \tag{28}$$

Since the intensity $I_{ee'}$ is real (equation (1)), equation (24) gives

$$c_{\mu rr'} = c^*_{\mu r' r}. \tag{29}$$

In some special symmetries (SS), it may be possible to write $c_{\mu rr'}$ in the factorised form

$$c_{\mu rr'} = a_r a^*_{r'} \qquad \text{(SS)} \tag{30}$$

so that the number of independent constants is reduced again:

$$c_{\mu r r} c_{\mu r' r'} = c_{\mu r r'} c_{\mu r' r} \qquad \text{(SS)}. \tag{31}$$

This will hold when the summations over ν, r_1 and r_3 in equation (21) reduce to a single term (for a given value of μ in either the symmetric or antisymmetric part of $1 \otimes 1$).

In all cases, equations (21), (24) imply that

$$c_{\mu rr'} = \varepsilon^\mu_r \varepsilon^\mu_{r'} c^*_{\mu^* r r'}. \tag{32}$$

Hence $c_{\mu rr'}$ is real if $r = r'$, and real/imaginary if $\mu = \mu^*$ as $\varepsilon^\mu_r \varepsilon^\mu_{r'} = \pm 1$. If $\mu \neq \mu^*$ and $r \neq r'$, $c_{\mu rr'}$ may be complex: this occurs only for $\mu = 1$, $(r, r') = (0, 1)$ in C_3, C_{3i}.

Another special symmetry of the intensity is that

$$I_{ee'}(\Omega) = I_{\tilde{e}\tilde{e}'}(\Omega) \qquad \text{(CU, NR)} \tag{33}$$

e.g. the intensity of scattering of right circularly polarised light (in and out) is equal to that of left circularly polarised light. This equation is true if

$$F_{\mu rr'}(e, e') = F_{\mu rr'}(\tilde{e}, \tilde{e}') \qquad \text{(CU)} \tag{34}$$

which from equations (27) to (28) is satisfied if $\mu = \mu^*$ and $r = r'$, i.e. if all the irreps $\mu \in [1 \otimes 1]_+$ are real and appear only once, and similarly in $[1 \otimes 1]_-$. (Equation (23) allows the symmetrisation here.) This holds for the cubic groups T_d, O, O_h (hence the label CU on equation (33)). It fails in T (since one μ is complex) and in lower symmetries since the identity irrep appears twice in $[1 \otimes 1]_+$ (both $x^2 + y^2$ and z^2 are invariants, and the term

$$F_{012}(e, e') \propto (e_x e'_x + e_y e'_y)(e_z e'_z)^*$$

for example does not satisfy equation (34)).

From equation (19), (26), we may write

$$I_{ee'}(\Omega) = \sum_{\rho\rho'\sigma\sigma'\mu rr'} e_\rho e'_{\rho'} \tilde{e}_\sigma \tilde{e}'_{\sigma'} T^{\mu rr'}_{\rho\rho'\sigma\sigma'} c_{\mu rr'} \tag{35}$$

$$T^{\mu rr'}_{\rho\rho'\sigma\sigma'} \equiv \sum_m \hat{\mu} \varepsilon^\mu_{r'} \begin{pmatrix} \mu \\ m \end{pmatrix} \begin{pmatrix} 1 & 1 & \mu^* \\ \rho & \rho' & m^* \end{pmatrix}^r \begin{pmatrix} 1 & 1 & \mu \\ \sigma & \sigma' & m \end{pmatrix}^{r'}. \tag{36}$$

Using equation (23), equation (46) in a cartesian basis (labelled by CAR), and the Derome–Sharp lemma we find the symmetries

$$T^{\mu rr'}_{\rho\rho'\sigma\sigma'} = \varepsilon^\mu_r \varepsilon^\mu_{r'} T^{\mu^* r' r}_{\sigma\sigma'\rho\rho'}$$

$$= T^{\mu rr'}_{\rho'\rho\sigma'\sigma} \qquad \text{(NR)} \tag{37}$$

$$= \varepsilon^\mu_r \varepsilon^\mu_{r'} (T^{\mu^* rr'}_{\rho\rho'\sigma\sigma'})^* \qquad \text{(CAR)}. \tag{38}$$

It follows from equations (32), (36) (see also Appendix 1) that

$$g_{\rho\rho'\sigma\sigma'} \equiv \sum_{\mu rr'} T^{\mu rr'}_{\rho\rho'\sigma\sigma'} c_{\mu rr'} \tag{39}$$

is always real. Hence we may re-define the group-theoretic parameters $T^{\mu rr'}_{\rho\rho'\sigma\sigma'}$ and physical constants $c_{\mu rr'}$ as real quantities $\tilde{T}^{\mu rr'}_{\rho\rho'\sigma\sigma'}$, $\tilde{c}_{\mu rr'}$:

$$g_{\rho\rho'\sigma\sigma'} = \sum_{(\mu rr')} \tilde{T}^{\mu rr'}_{\rho\rho'\sigma\sigma'} \tilde{c}_{\mu rr'} \tag{40}$$

$$\tilde{T}^{\mu rr'}_{\rho\rho'\sigma\sigma'} \equiv \theta^\mu_{rr'} (T^{\mu rr'}_{\rho\rho'\sigma\sigma'} + (2 - \delta_{\mu\mu^*} - \delta_{rr'}) \varepsilon^\mu_r \varepsilon^\mu_{r'} T^{\mu^* r' r}_{\rho\rho'\sigma\sigma'}) \tag{41a}$$

$$\tilde{c}_{\mu rr'} = (\theta^\mu_{rr'})^* c_{\mu rr'}.$$

These definitions cover $\mu = \mu^*$ and/or $r = r'$, with $\theta^\mu_{rr'} \equiv 1$ (i) as $\varepsilon^\mu_r \varepsilon^\mu_{r'} = +1(-1)$. The exceptional case, $\mu = 1$ of $G = C_3, C_{3i}$, where the constants c_{101}, c_{110} are complex, is given by ($\varepsilon^1_0 \varepsilon^1_1 = 1$):

$$\tilde{T}^{101}_{\rho\rho'\sigma\sigma'} \equiv 2\mathrm{Re}(T^{101}_{\rho\rho'\sigma\sigma'} + T^{-110}_{\rho\rho'\sigma\sigma'})$$

$$\tilde{T}^{110}_{\rho\rho'\sigma\sigma'} \equiv 2\mathrm{Im}(T^{101}_{\rho\rho'\sigma\sigma'} + T^{-110}_{\rho\rho'\sigma\sigma'}) \tag{41b}$$

and $\tilde{c}_{101} \equiv \mathrm{Re}\, c_{101}$, $\tilde{c}_{110} = -\mathrm{Im}\, c_{101}$. Equation (30) then gives $(\tilde{c}_{101})^2 + (\tilde{c}_{110})^2 = \tilde{c}_{100}\tilde{c}_{111}$. The summation in equation (40) need then be taken only over a restricted set of values of $\mu rr'$, corresponding to those tabulated later. Also, since equation (41) satisfies

$$\tilde{T}^{\mu rr'}_{\rho\rho'\sigma\sigma'} = \tilde{T}^{\mu rr'}_{\sigma\sigma'\rho\rho'} = \tilde{T}^{\mu rr'}_{\rho'\rho\sigma'\sigma} \qquad \text{(NR)} \tag{42}$$

only 27 different sets of polarisation labels $\rho\rho'\sigma\sigma'$ need be considered.

In table 2 we list all independent sets of constants $\tilde{T}^{\mu rr'}_{\rho\rho'\sigma\sigma'}$ for all point groups; a factor $\hat{\mu}$ is included for ease of tabulation. Table 3 specifies which set of $\tilde{T}^{\mu rr'}_{\rho\rho'\sigma\sigma'}$ is appropriate for any choice of point group, electronic and phonon symmetry, also whether $\tilde{c}_{\mu rr'}$ is factorisable in the sense of equations (30), (31).

We illustrate the application of tables 2 and 3 to a system with symmetry $G = O$, electronic symmetry Λ and phonon symmetry κ both equal to $2(E, \Gamma_3)$. Table 3 shows that only $(\mu rr') = (000), (200)$ are required, i.e., equation (35) becomes

$$I_{ee'}(\Omega) = \sum_{\rho\rho'\sigma\sigma'} (\tilde{T}^{000}_{\rho\rho'\sigma\sigma'} \tilde{c}_{000} + \tilde{T}^{200}_{\rho\rho'\sigma\sigma'} \tilde{c}_{200}) e_\rho e'_{\rho'} \tilde{e}_\sigma \tilde{e}'_{\sigma'}.$$

Table 2. Independent sets of constants $\mu\tilde{l}\tilde{l}'^{\mu rr'}_{\rho\rho'\sigma\sigma'}$. Columns are labelled in conformity with table 3, which indicates which column(s) is (are) relevant for a given physical system. The rows labelled *zzyz* and *zzzx* are omitted, as they are identically zero, as are columns O–Z (top half) and C–L (bottom half).

$\rho\rho'\sigma\sigma'$	A	B	C	D	E	F	G	H	I	J	K	L	M	N
xxxx	$\frac{2}{3}$	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{-\sqrt{2}}{3}$	$\frac{1}{6}$	$\frac{2}{3}$	$\frac{-2}{\sqrt{6}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{2}$	—	—	—	—	—
xxyy	$\frac{-1}{3}$	$\frac{-1}{2}$	$\frac{1}{3}$	$\frac{-\sqrt{2}}{3}$	$\frac{1}{6}$	$\frac{-1}{3}$	—	—	$\frac{-1}{2}$	—	—	—	—	—
xxzz	$\frac{-1}{3}$	—	$\frac{1}{3}$	$\frac{1}{3\sqrt{2}}$	$\frac{-1}{3}$	$\frac{-1}{3}$	$\frac{-1}{\sqrt{6}}$	$\frac{-1}{\sqrt{3}}$	—	—	—	—	—	—
xxxy	—	—	—	—	—	—	—	—	—	$\frac{1}{2\sqrt{3}}$	$\frac{-1}{\sqrt{6}}$	$\frac{-1}{2}$	—	—
xxyz	—	—	—	—	—	—	—	—	—	—	—	—	$\frac{1}{2}$	—
xxzx	—	—	—	—	—	—	—	—	—	—	—	—	—	$\frac{1}{2}$
yyyy	$\frac{2}{3}$	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{-\sqrt{2}}{3}$	$\frac{1}{6}$	$\frac{2}{3}$	$\frac{2}{\sqrt{6}}$	$\frac{-1}{\sqrt{3}}$	$\frac{1}{2}$	—	—	—	—	—
yyzz	$\frac{-1}{3}$	—	$\frac{1}{3}$	$\frac{1}{3\sqrt{2}}$	$\frac{-1}{3}$	$\frac{-1}{3}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{3}}$	—	—	—	—	—	—
yyxy	—	—	—	—	—	—	—	—	—	$\frac{1}{2\sqrt{3}}$	$\frac{-1}{\sqrt{6}}$	$\frac{1}{2}$	—	—
yyyz	—	—	—	—	—	—	—	—	—	—	—	—	$\frac{-1}{2}$	—
yyzx	—	—	—	—	—	—	—	—	—	—	—	—	—	$\frac{-1}{2}$
zzzz	$\frac{2}{3}$	—	$\frac{1}{3}$	$\frac{2\sqrt{2}}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	—	—	—	—	—	—	—	—
zzxy	—	—	—	—	—	—	—	—	—	$\frac{-1}{\sqrt{3}}$	$\frac{-1}{\sqrt{6}}$	—	—	—

	A	B	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z
xyxy	$\frac{1}{2}$	$\frac{1}{2}$	—	—	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	—	—	—	—	—	—	—	—
xyyx	$\frac{1}{2}$	$\frac{1}{2}$	—	—	$\frac{1}{2}$	$\frac{-1}{2}$	$\frac{1}{2}$	$\frac{-1}{2}$	—	—	—	—	—	—	—	—
xyyz	—	—	—	$\frac{-1}{2}$	—	—	—	—	—	—	—	—	—	—	—	—
xyzy	—	—	—	$\frac{-1}{2}$	—	—	—	—	—	—	—	—	—	—	—	—
xyzx	—	—	$\frac{1}{2}$	—	—	—	—	—	—	—	—	—	—	—	—	—
xyxz	—	—	$\frac{1}{2}$	—	—	—	—	—	—	—	—	—	—	—	—	—
yzyz	$\frac{1}{2}$	—	—	—	$\frac{1}{2}$	$\frac{1}{2}$	—	—	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	—	—	—	—
yzzy	$\frac{1}{2}$	—	—	—	$\frac{1}{2}$	$\frac{-1}{2}$	—	—	$\frac{1}{2}$	$\frac{-1}{2}$	$\frac{1}{2}$	$\frac{-1}{2}$	—	—	—	—
yzzx	—	—	—	—	—	—	—	—	—	—	—	—	$\frac{-1}{2}$	$\frac{1}{2}$	—	—
yzxz	—	—	—	—	—	—	—	—	—	—	—	—	$\frac{-1}{2}$	$\frac{-1}{2}$	—	—
zxzx	$\frac{1}{2}$	—	—	—	$\frac{1}{2}$	$\frac{1}{2}$	—	—	$\frac{1}{2}$	$\frac{1}{2}$	—	—	—	—	$\frac{1}{2}$	$\frac{1}{2}$
zxxz	$\frac{1}{2}$	—	—	—	$\frac{1}{2}$	$\frac{-1}{2}$	—	—	$\frac{1}{2}$	$\frac{-1}{2}$	—	—	—	—	$\frac{1}{2}$	$\frac{-1}{2}$

Table 3. Raman scattering symmetries for all electronic, phonon and point-group symmetries. The first three rows list μ, r, r' (for the definition of the parentage labels r, r', see table A1); the fourth row specifies which column of table 2 is relevant for the given choice of coupling symmetry. If $|\Lambda| = 1$, the relevant rows are those labelled $\Lambda = 0$. An entry of 1 specifies that the corresponding constant $\tilde{c}_{\mu rr'}$ is non-zero; the asterisk, when present, indicates that the constant $c_{\mu rr'}$ is factorisable (equation (30)). Phonons not listed for any Λ are not Raman active for that choice of Λ.

C_2, C_s, C_{2h}

		$\mu=$	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1
		$r=$	0	0	0	1	1	1	2	2	3	4	0	0	1	2	2	3
		$r'=$	0	1	2	3	1	2	3	2	3	3	4	0	1	1	2	3	3
Λ	κ		C	D	K	G	E	J	H	Q	L	I	R	Y	W	U	Z	X	V
0	0		1*	1*	1*	1*	1*	1*	1*	1*	1*	1*	—	—	—	—	—	—	—
	1		—	—	—	—	—	—	—	—	—	—	—	1*	1*	1*	—	—	—
$\pm\frac{1}{2}$	0		1*	1*	1*	1*	1*	1*	1*	1*	1*	1*	1*	—	—	—	1	1	1
	1		—	—	—	—	—	—	—	—	—	—	1	1*	1*	1*	1	1	1

C_3, C_{3i}

		$\mu=$	0	0	0	0	1	1	1	1	1
		$r=$	0	0	1	2	0	0	1	1	2
		$r'=$	0	1	1	2	0	1	0	1	2
Λ	κ		C	D	E	R	B	N	M	S	T
0	0		1*	1*	1*	—	—	—	—	—	—
	±1		—	—	—	—	1*	1*	1*	1*	—
$\pm\frac{1}{2}$	0		1*	1*	1*	1*	—	—	—	—	1*
	±1		—	—	—	1	1*	1*	1*	1*	1
±1	0		1*	1*	1*	1*	1*	1*	1*	1*	—
	±1		1	1	1	—	1	1	1	1	1*

C_4, C_{4h}, S_4

		$\mu=$	0	0	0	0	2	2	2	1	1
		$r=$	0	0	1	2	0	0	1	0	1
		$r'=$	0	1	1	2	0	1	1	0	1
Λ	κ		C	D	E	R	I	L	Q	S	T
0	0		1*	1*	1*	—	—	—	—	—	—
	±1		—	—	—	—	—	—	—	1*	—
	2		—	—	—	—	1*	1*	1*	—	—
$\pm\frac{1}{2}$, $\pm\frac{3}{2}$	0		1*	1*	1*	1*	—	—	—	—	1*
	±1		—	—	—	1	—	—	—	1*	1
	2		—	—	—	—	1*	1*	1*	—	1*
±1	0		1*	1*	1*	1*	1	1	1	—	—
	±1		—	—	—	—	—	—	—	1	1*
	2		1	1	1	—	1	1	1	—	—

Table 3—continued

C_6, C_{6h}, C_{3h}

		$\mu=$	0	0	0	0	2	1	1
		$r=$	0	0	1	2	0	0	1
		$r'=$	0	1	1	2	0	0	1
Λ	κ		C	D	E	R	B	S	T
0	0		1*	1*	1*	—	—	—	—
	±1		—	—	—	—	—	1*	—
	±2		—	—	—	—	1*	—	—
$\pm\frac{1}{2}$, $\pm\frac{5}{2}$	0		1*	1*	1*	1*	—	—	1*
	±1		—	—	—	1	—	1*	1
	±2		—	—	—	—	1*	—	1*
±1, ±2	0		1*	1*	1*	1*	1*	—	—
	±1		—	—	—	—	—	1	1*
	±2		1	1	1	—	1	—	—
	3		—	—	—	—	—	1*	—
$\pm\frac{3}{2}$	0		1*	1*	1*	1*	—	—	—
	±1		—	—	—	—	—	1*	1*
	±2		—	—	—	—	1*	—	1
	3		—	—	—	1	—	—	—

D_2, D_{2h}, C_{2v}

	$\mu=0$	0	0	0	0	0	$\tilde{0}$	$\tilde{0}$	1	1	$\tilde{1}$	$\tilde{1}$
	$r=0$	0	0	1	1	2	0	1	0	1	0	1
	$r'=0$	1	2	1	2	2	0	1	0	1	0	1
Λ	κ	C	D	G	E	H	I	Q	R	Y	Z	U	V
0	0	1*	1*	1*	1*	1*	1*	—	—	—	—	—	—
	$\tilde{0}$	—	—	—	—	—	—	1*	—	—	—	—	—
	1	—	—	—	—	—	—	—	—	1*	—	—	—
	$\tilde{1}$	—	—	—	—	—	—	—	—	—	—	1*	—
$\frac{1}{2}$	0	1*	1*	1*	1*	1*	1*	—	1*	—	1*	—	1*
	$\tilde{0}$	—	—	—	—	—	—	1*	—	—	1*	—	1*
	1	—	—	—	—	—	—	—	1*	1*	—	—	1*
	$\tilde{1}$	—	—	—	—	—	—	—	1*	—	1*	1*	—

D_3, C_{3v}, D_{3d}

	$\mu=$	0	0	0	1	1	1	1	$\tilde{0}$
	$r=$	0	0	1	0	0	1	2	0
	$r'=$	0	1	1	0	1	1	2	0
Λ	κ	C	D	E	B	N	S	T	R
0	0	1*	1*	1*	—	—	—	—	—
	1	—	—	—	1*	1*	1*	—	—
$\frac{1}{2}$	0	1*	1*	1*	—	—	—	1*	1*
	$\tilde{0}$	—	—	—	—	—	—	1*	—
	1	—	—	—	1*	1*	1*	1	1*
1	0	1*	1*	1*	1*	1*	1*	—	1*
	$\tilde{0}$	—	—	—	1*	1*	1*	—	—
	1	1*	1*	1*	1	1	1	1*	—
$\pm\frac{3}{2}$	0	1*	1*	1*	—	—	—	—	1
	$\tilde{0}$	—	—	—	—	—	—	—	1
	1	—	—	—	1*	1*	1*	1	—

Table 3—continued

D_4, D_{2d}, D_{4h}, C_{4v}

	$\mu =$	0	0	0	2	$\bar{2}$	1	1	$\bar{0}$
	$r =$	0	0	1	0	0	0	1	0
	$r' =$	0	1	1	0	0	0	1	0
Λ	κ	C	D	E	I	Q	S	T	R
0	0	1*	1*	1*	—	—	—	—	—
	1	—	—	—	—	—	1*	—	—
	2	—	—	—	1*	—	—	—	—
	$\bar{2}$	—	—	—	—	1*	—	—	—
$\frac{1}{2}, \frac{3}{2}$	0	1*	1*	1*	—	—	—	1*	1*
	$\bar{0}$	—	—	—	—	—	—	1*	—
	1	—	—	—	—	—	1*	1*	1*
	2	—	—	—	1*	—	—	1*	—
	$\bar{2}$	—	—	—	—	1*	—	1*	—
1	0	1*	1*	1*	1*	1*	—	—	1*
	$\bar{0}$	—	—	—	1*	1*	—	—	—
	1	—	—	—	—	—	1	1*	—
	2	1*	1*	1*	1*	—	—	—	—
	$\bar{2}$	1*	1*	1*	—	1*	—	—	—

D_6, D_{3h}, D_{6h}, C_{6v}

	$\mu =$	0	0	0	2	1	1	$\bar{0}$
	$r =$	0	0	1	0	0	1	0
	$r' =$	0	1	1	0	0	1	0
Λ	κ	C	−D	E	B	S	T	R
0	0	1*	1*	1*	—	—	—	—
	1	—	—	—	—	1*	—	—
	2	—	—	—	1*	—	—	—
$\frac{1}{2}, \frac{5}{2}$	0	1*	1*	1*	—	—	1*	1*
	$\bar{0}$	—	—	—	—	—	1*	—
	1	—	—	—	—	1*	1*	1*
	2	—	—	—	1*	—	1*	—
1, 2	0	1*	1*	1*	1*	—	—	1*
	$\bar{0}$	—	—	—	1*	—	—	—
	1	—	—	—	—	1	1*	—
	2	1*	1*	1*	1	—	—	—
	3, $\bar{3}$	—	—	—	—	1*	—	—
$\frac{3}{2}$	0	1*	1*	1*	—	—	—	1*
	1	—	—	—	—	1*	1*	—
	2	—	—	—	1*	—	1	—
	3, $\bar{3}$	—	—	—	—	—	—	1*

Table 3—continued

T, T_h

	$\mu=$	0	2	1	1
	$r=$	0	0	0	1
	$r'=$	0	0	0	1
Λ	κ	C	F	O	P
0	0	1*	—	—	—
	1	—	—	1*	—
	±2	—	1*	—	—
$\frac{1}{2}$	0	1*	—	—	1*
	1	—	—	1*	1
	±2	—	1*	—	1
1	0	1*	1*	1*	1*
	1	1*	1	1	1
	±2	1	1	1	1
$\pm\frac{3}{2}$	0	1*	1*	1*	1
	1	1*	1	1	1
	±2	1	1	1	1
±2	0	1*	1*	—	—
	1	—	—	1	1*
	±2	1	1	—	—

O, O_h, T_d

	$\mu=$	0	2	$\tilde{1}$	1
	$r=$	0	0	0	0
	$r'=$	0	0	0	0
Λ	κ	C	F	O	P
0	0	1*	—	—	—
	2	—	1*	—	—
	$\tilde{1}$	—	—	1*	—
$\frac{1}{2}, \tilde{\frac{1}{2}}$	0	1*	—	—	1*
	1	—	—	—	1*
	2	—	1*	—	1*
	$\tilde{1}$	—	—	1*	1*
1, $\tilde{1}$	0	1*	1*	1*	1*
	1	—	1	1	1*
	2, $\tilde{1}$	1*	1	1	1*
	$\tilde{0}$	—	1*	—	—
$\frac{3}{2}$	0	1*	1*	1*	1
	1	—	1	1	1
	2, $\tilde{1}$	1*	1	1	1
	$\tilde{0}$	—	1*	—	1*
2	0	1*	1*	—	—
	1	—	—	1	—
	2	1*	1	—	—
	$\tilde{1}$	—	—	1	1*
	$\tilde{0}$	—	1*	—	—

K

	$\mu=$	0	1	2
	$r=$	0	0	0
	$r'=$	0	0	0
Λ	κ	C	P	A
0	0	1*	—	—
	2	—	—	1*
$\frac{1}{2}$	0	1*	1*	—
	1	—	1*	—
	2	—	1*	1*
1	0	1*	1*	1*
	1	—	1*	1
	2	1*	1*	1
	3	—	—	1
	$\tilde{1}$	—	—	1*
$\frac{3}{2}$	0	1*	1*	1*
	1	—	1*	1
	2	1*	1	1
	3	—	1	1
	$\tilde{\frac{1}{2}}$	—	1*	1*
2	0	1*	1*	1
	1, $\tilde{1}$	—	1*	1
	2	1	1	1
	3	1*	1	1
$\frac{5}{2}$	0	1*	1	1
	1, $\tilde{1}$	—	1	1
	2	1	1	1
	3	1*	1	1
3	0	1*	1*	1*
	1	—	1*	1
	2	1*	1	1
	3	1*	1*	1
	$\tilde{1}$	—	—	1
$\tilde{1}$	0	1*	—	1*
	1	—	—	1
	2	1*	1*	1
	3	—	1*	1
	$\tilde{1}$	—	—	1*
$\tilde{\frac{1}{2}}$	0	1*	—	—
	2	—	1*	1*
	3	—	1*	—

The constants $\hat{0}\tilde{T}^{000}_{\rho\rho'\sigma\sigma'}$, $\hat{2}\tilde{T}^{200}_{\rho\rho'\sigma\sigma'}$ are given in columns C, F of table 2; other related constants ($\rho\rho' \rightleftharpoons \sigma\sigma'$; $\rho \rightleftharpoons \rho'$, $\sigma \rightleftharpoons \sigma'$) are obtained using equation (42). This yields in this example:

$$I_{ee'}(\Omega) = (1/3\sqrt{2})\,[(\sqrt{2}\,\tilde{c}_{000} + 2\tilde{c}_{200})\,(e_x e'_x \tilde{e}_x \tilde{e}'_x + e_y e'_y \tilde{e}_y \tilde{e}'_y + e_z e'_z \tilde{e}_z \tilde{e}'_z) + (\sqrt{2}\tilde{c}_{000} - \tilde{c}_{200})\,(e_x e'_x \tilde{e}_y \tilde{e}'_y + e_y e'_y \tilde{e}_x \tilde{e}'_x + e_x e'_x \tilde{e}_z \tilde{e}'_z + e_z e'_z \tilde{e}_x \tilde{e}'_x + e_y e'_y \tilde{e}_z \tilde{e}'_z + e_z e'_z \tilde{e}_y \tilde{e}'_y)].$$

Thus, given the polarisation choice $\boldsymbol{e} = (1/\sqrt{2})(1, \mathrm{i}, 0) = \boldsymbol{e}'$, the intensity is proportional to $\tilde{c}_{200}$. Two such measurements determine the polarisation dependence completely.

The extent to which symmetry assignments may be made for either the electronic (Λ) or phonon (κ) symmetry is apparent from table 3. Irreps with identical Kronecker product rules (equation (16)) certainly cannot be distinguished by this technique, and are tabulated together. In addition, certain combinations of Λ, κ may give the same symmetries in the constant $\tilde{T}_{\rho\rho'\sigma\sigma'}$ and thus be indistinguishable. For example, in the case $G = \mathrm{O}$ and $\Lambda = 1(\Gamma_4)$, the phonons $\kappa = 2(\Gamma_3)$ and $\tilde{1}(\Gamma_5)$ cannot be distinguished by their Raman spectral polarisation behaviour; however, they could be so distinguished if the ground state were $\Lambda = \frac{1}{2}(\Gamma_6)$ or $\frac{1}{2}(\Gamma_7)$. In no case does a phonon mode which is Raman active (for $|\Lambda| = 1$) become inactive for some other choice of Λ. Indeed, any phonon symmetry κ becomes Raman active for some choice of Λ.

4. Orientationally averaged scattering centres

Much work on phonon Raman spectroscopy is performed on powders or vapours, in which the relative orientation of the Stokes vector for either light beam and the symmetry axes of the scatterer is distributed over all possible values uniformly. The analysis of § 2 may be adapted for this case, mainly by replacing the irrep label μ of the point group G by that of the full rotation group R_3 (or SO_3). Equation (19) becomes

$$I_{ee'}(\Omega) = \sum_j F_j(\boldsymbol{e}, \boldsymbol{e}')\, c_j \tag{43}$$

with

$$F_j(\boldsymbol{e}, \boldsymbol{e}') = \sum_m f[\boldsymbol{e}\boldsymbol{e}']^j_m\, ([\boldsymbol{e}\boldsymbol{e}']^j_m)^* \tag{44}$$

$$c_j = \sum_{kll'm} f \left| \sum_{\rho\rho'} \begin{pmatrix} 1 & 1 & j \\ \rho & \rho' & m \end{pmatrix}^* R^{kll'}_{\rho\rho'}(\Omega) \right|^2. \tag{45}$$

The simplest proof of these results is to consider a rotation of all photon polarisation vectors in equation (1) by a general element of the group SO_3, then to average this element over the group. A generalised group orthogonality theorem, akin to the Wigner–Eckart theorem, then immediately reduces the answer to equations (43)–(45). This procedure may be illustrated using the graphical approach to angular momentum, as in figure 1. The group operator notation etc is that of Stedman (1975) (Appendix 1). The use of this method of proof in previous work is reviewed in the Introduction.

The results of equations (43)–(45) are well known at least for non-degenerate scatterers since the early work of Placzek in 1934 (Placzek 1962). We may calculate the

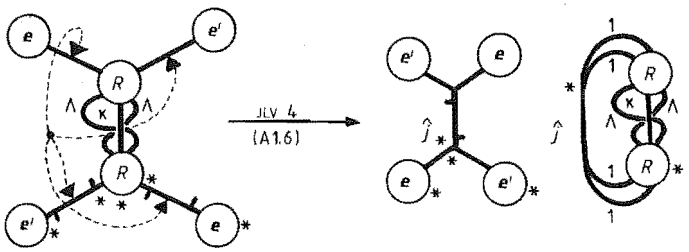


Figure 1. Raman spectrum for orientationally averaged scatterers; proof of equation (43).

coupled tensors in these equations as in table 4, using the fundamental properties of the $3j$ symbols, e.g. their unitarity and such results as (in the cartesian basis given in § 3)

$$\begin{pmatrix} 1 & 1 \\ \alpha & \beta \end{pmatrix} = \delta_{\alpha\beta} \tag{46}$$

$$\begin{pmatrix} 1 & 1 & 1 \\ \alpha & \beta & \gamma \end{pmatrix} = \frac{1}{\sqrt{6}} \varepsilon_{\alpha\beta\gamma}.$$

Table 4 is in agreement with the Placzek formulation; the constants c_j are related to his G^0 (invariant scattering, $j = 0$), G^a (antisymmetric scattering, $j = 1$) and G^s (symmetric traceless scattering, $j = 2$).

It follows from table 4 that the geometry of any experiment is adequately specified by the two parameters $|e \cdot e'|$, $|e \cdot e'^*|$. McClain (1971) uses this to unify the analysis of different two-photon or Raman scattering experiments. Two measurements suffice to determine the response of the system under all conditions, i.e. the relative sizes of the constants c_j; it is only necessary to ensure that the measurements involve different proportions of $|e \cdot e'|$ and $|e \cdot e'^*|$. Customarily these measurements are taken to be the depolarisation ratio and the reversal ratio (Suschinskii 1972). McClain (1971) did not clarify the connection between his constants and those of Placzek (1962); the connection is apparent from table 4:

$$\begin{aligned} G^0 &= c_0 = \tfrac{1}{3}\delta f \\ G^a &= \sqrt{3}c_1 = \tfrac{1}{2}(\delta g - \delta h) \\ G^s &= \sqrt{5}c_2 = \tfrac{1}{2}(\delta g + \delta h) - \tfrac{1}{3}\delta f. \end{aligned} \tag{47}$$

For example, if the ground state is non-degenerate ($|\Lambda| = 1$) and the non-resonant limit is taken, equation (3) shows that there is no antisymmetric scattering ($c_1 = 0$).

Table 4. Geometrical factors for orientationally averaged Raman scatterers.

j	$F_j(e, e')$
0	$\frac{1}{3}\lvert e \cdot e' \rvert^2$
1	$\frac{1}{2\sqrt{3}}\lvert e \times e' \rvert^2 = \frac{1}{2\sqrt{3}}(1 - \lvert e \cdot e'^* \rvert^2)$
2	$\frac{1}{\sqrt{5}}(\frac{1}{2} - \frac{1}{3}\lvert e \cdot e' \rvert^2 + \frac{1}{2}\lvert e \cdot e'^* \rvert^2)$

Table 5. Values of phonon symmetry κ for which the coefficients $c_j(\Lambda, \kappa, \Omega)$ are non-zero for orientationally averaged scatterers. The rows $\Lambda = 0$ cover all electronic symmetries Λ for which $|\Lambda| = 1$.

G	$j =$ / Λ	0	1	2
C_1				
	0	0	—	0
C_2, C_s, C_{2h}				
	0	0	—	0, 1
	$\pm\frac{1}{2}$	0	0, 1	0, 1
C_3, S_6				
	0	0	—	0, ±1
	±1	0, ±1	0, ±1	0, ±1
	$\pm\frac{1}{2}$	0	0, ±1	0, ±1
C_4, C_{4h}, S_4				
	0	0	—	0, ±1, ±2
	±1	0, 2	0, ±1	0, ±1, 2
	$\pm\frac{1}{2}$, $\pm\frac{3}{2}$	0	0, ±1, 2	0, ±1, 2
C_6, C_{3h}, C_{6h}				
	0	0	—	0, ±1, ±2
	±1, ±2	0, ±2	0, ±1	0, ±1, ±2, 3
	$\pm\frac{1}{2}$, $\pm\frac{5}{2}$	0	0, ±1, ±2	0, ±1, ±2
	$\pm\frac{3}{2}$	0	0, ±1, ±2, 3	0, ±1, ±2
D_2, D_{2h}, C_{2v}				
	0	0	—	0, $\tilde{0}$, 1, $\tilde{1}$
	$\frac{1}{2}$	0	0, $\tilde{0}$, 1, $\tilde{1}$	0, $\tilde{0}$, 1, $\tilde{1}$
D_3, C_{3v}, D_{3d}				
	0	0	—	0, 1
	$\frac{1}{2}$	0	0, $\tilde{0}$, 1	0, 1
	1	0, 1	1	0, $\tilde{0}$, 1
	$\pm\frac{3}{2}$	0	0, $\tilde{0}$, 1	0, 1
D_4, C_{4v}, D_{2d}, D_{4h}				
	0	0	—	0, 1, 2, $\tilde{2}$
	1	0, 2, $\tilde{2}$	0, 1	0, $\tilde{0}$, 1, 2, $\tilde{2}$
	$\frac{1}{2}$, $\frac{3}{2}$	0	0, $\tilde{0}$, 1, 2, $\tilde{2}$	0, 1, 2, $\tilde{2}$
D_6, C_{6v}, D_{3h}, D_{6h}, $C_{\infty v}$, $D_{\infty h}$				
	0	0	—	0, 1, 2
	1, 2	0, 2	0, 1	0, $\tilde{0}$, 1, 2, 3, $\tilde{3}$
	$\frac{1}{2}$, $\frac{5}{2}$	0	0, $\tilde{0}$, 1, 2	0, 1, 2
	$\frac{3}{2}$	0	0, 1, 2, 3, $\tilde{3}$	0, 1, 2
T, T_h				
	0	0	—	1, ±2
	±2	0, ±2	1	0, 1, ±2
	1, $\pm\frac{3}{2}$	0, 1, ±2	0, 1, ±2	0, 1, ±2
	$\frac{1}{2}$	0	0, 1, ±2	1, ±2
O, O_h, T_d				
	0	0	—	$\tilde{1}$, 2
	2	0, 2	$\tilde{1}$	0, $\tilde{0}$, 1, $\tilde{1}$, 2
	1, $\tilde{1}$	0, $\tilde{1}$, 2	0, 1, $\tilde{1}$, 2	0, $\tilde{0}$, 1, $\tilde{1}$, 2
	$\frac{1}{2}$, $\frac{7}{2}$	0	0, 1, $\tilde{1}$, 2	$\tilde{1}$, 2
	$\frac{3}{2}$	0, $\tilde{1}$, 2	0, $\tilde{0}$, 1, $\tilde{1}$, 2	0, $\tilde{0}$, 1, $\tilde{1}$, 2
K				
	0	0	—	2
	$\frac{1}{2}$	0	0, 1, 2	2
	1	0, 2	1, 2	0, 1, $\tilde{1}$, 2, 3
	$\frac{3}{2}$	0, 2	0, 1, $\tilde{1}$, 2, 3	0, 1, $\tilde{1}$, 2, 3
	2, $\frac{5}{2}$	0, 2, 3	0, 1, $\tilde{1}$, 2, 3	0, 1, $\tilde{1}$, 2, 3
	3	0, 2, 3	0, 1, 2, 3	0, 1, $\tilde{1}$, 2, 3
	$\tilde{1}$	0, 2	2, 3	0, 1, $\tilde{1}$, 2, 3
	$\frac{7}{2}$	0	2, 3	2

As in this illustration, the choice of G, Λ and κ restricts some constants c_j to be zero and thus limits the possible dependences of the Raman spectrum on experimental arrangement. McClain (1971) gives a full discussion for non-degenerate states. Child (1963) lists the combinations of G, Λ and κ for which Λ is a spin irrep and $c_1 \neq 0$. We give a general tabulation (based on applying equation (16) with $\mu \rightarrow j$) in table 5. In particular we include corrections to Child (1963), namely the inclusion of some phonon symmetries (e.g. $\kappa = \Gamma_5$ for $G = C_{4v}$ and $\Lambda = \Gamma_6$) which can induce antisymmetric scattering.

Our calculation agrees with that of Child (1963) in predicting a term $c_1 \neq 0$ for $G = T_d$, $\Lambda = \Gamma_3$ and $\kappa = \Gamma_5$. This result is contradicted by Parameswaram *et al* (1977) who use an alternative approach (Koningstein 1975, Koningstein and Parameswaram 1976). We are unconvinced by the arguments of these authors. Their analysis of Kronecker products and of spin dependence of contributions to a scattering amplitude is adequately covered by the work of Child (1963) and by this work without recourse to an explicit subgroup basis, as used by Koningstein and Parameswaram. The only reason for any difference in conclusions appears to be that in Koningstein (1975) and following papers contributions to the scattering amplitude that would have corresponded in a sufficiently lower symmetry to joint electronic and vibrational, rather than purely vibrational, Raman transitions are neglected. We see no justification for the removal of any subset of contributions to the scattering amplitude.

5. Alternative recoupling scheme

Thus far in our development we have followed Placzek (1962) and most subsequent authors by coupling the photon interaction operators for different photons first, thus gaining the coupling symmetry label μ or j (equation (7), (22), (44)). In quantum beat spectroscopy (e.g. Dodd and Series 1978) it is customary to couple the operators for the same photon first. We now consider the relative merits of this approach.

Consider first the case of orientationally averaged scatterers (§ 4). The orthogonality theorem used in figure 1 could have been used in the manner shown in figure 2, essentially by virtue of a recoupling procedure (or $6j$ symbol). Equation (37) would then become

$$I_{ee'}(\Omega) = \sum_k F'_k(e, e')\, c'_k \tag{48}$$

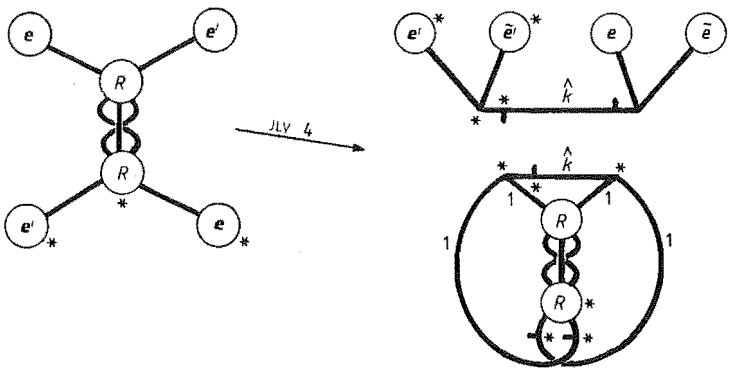


Figure 2. Raman spectrum for orientationally averaged scatterers: proof of the alternative coupling of equation (48).

Table 6. Geometrical factors for orientationally averaged scatterers in an alternative coupling.

k	$F_k^l(e, e')$
0	$\frac{1}{3}$
1	$\frac{1}{2\sqrt{3}}(e \times e^*) \cdot (e' \times e'^*)$
	$= \frac{1}{2\sqrt{3}}(\lvert e \cdot e' \rvert^2 - \lvert e \cdot e'^* \rvert^2)$
2	$\frac{1}{\sqrt{5}}(\frac{1}{2}(\lvert e \cdot e'^* \rvert^2 + \lvert e \cdot e' \rvert^2) - \frac{1}{3})$

with

$$F_k^l(e, e') = \sum_q \hat{k}[e\, e]_q^k ([\tilde{e}'\, e']_q^k)^* \tag{49}$$

$$c_k^l = \sum_j \hat{j}\hat{k} \begin{Bmatrix} j & 1 & 1 \\ k & 1 & 1 \end{Bmatrix} (-1)^j c_j. \tag{50}$$

On inserting equation (46) into equation (49), we find explicit forms for the geometrical factors $F_k^l(e, e')$ as in table 6. The $k = 0$ term is isotropic, and the $k = 1$ term vanishes in linear polarisation, when $\tilde{e} = e$. If e and e' are identical except for a rotation specified by Euler angles α, β, γ, $F_k^l(e, e') \propto P_k(\cos\beta)$ (Dodd and Series 1978).

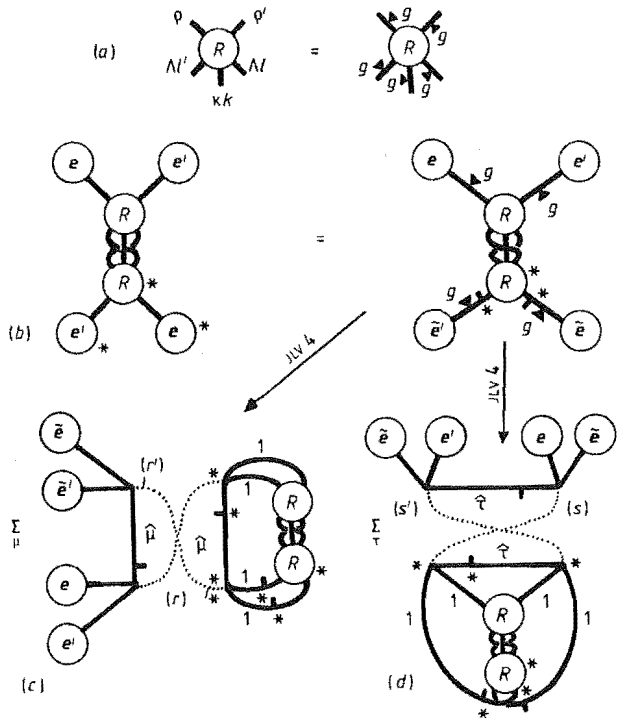


Figure 3. Raman spectrum for oriented scatterers: (*a*) invariance of the scattering amplitude under group operations; (*b*) group-theoretic structure of equation (1); (*c*), (*d*) reduction of the intensity in alternative couplings (equations (19), (51)).

This recoupling has obvious advantages in problems in which the symmetry of intermediate states is of interest. For example, in the case of resonance fluorescence, the term $k = 0$ does not contribute to quantum beats (Dodd and Series 1978). The latter involve interference between hyperfine levels of differing energy and rotational symmetry; if $k = 0$, any intermediate state must have the same symmetry as the initial state. We may therefore anticipate an advantage in Raman scattering situations when the intermediate state symmetry is restricted, e.g. resonant Raman scattering. However, even in this case no great advantage is associated with orientational averaging unless the energy eigenstates have well defined angular momentum.

Consider now the situation for oriented scatterers. First we note that equation (19), which expresses the Raman scattering intensity as the product of geometrical and physical factors, may be derived from equation (1) using the basic property of the invariance of the Raman scattering amplitude under point group operations (figure 3*a*) together with the techniques of § 4 in the point group generalisation of Appendix 1. This alternative procedure is summarised in figure 3(*b*)–(*c*). Now the last step, utilising the group orthogonality theorem JLV 4, could have been re-expressed as in figure 3(*d*). This corresponds to the alternative coupling described above for orientationally averaged scatterers. Equation (19) has an analogue

$$I_{ee'}(\Omega) = \sum_{\tau ss'} F'_{\tau ss'}(e, e')c'_{\tau ss'} \tag{51}$$

with

$$F'_{\tau ss'}(e, e') = \sum_t \hat{t}[\tilde{e}\, e]_t^{\tau s}([\tilde{e}'\, e']_t^{\tau s'})^* \tag{52}$$

$$c'_{\tau ss'} = \sum_{\mu rr'} \hat{\mu}\hat{\tau}\varepsilon_r^{\mu}\varepsilon_s^{\tau}\{11\mu r\}\begin{Bmatrix}\mu & 1 & 1\\ \tau^* & 1 & 1\end{Bmatrix}_{r's'sr} c_{\mu rr'}. \tag{53}$$

The 6*j* symbol in this expression is reducible in the sense of § 2, i.e. it is expressible in terms of reducible 3*jm* symbols in the same manner that standard 6*j* symbols are expresssible in terms of 3*jm* symbols. Equations (48)–(50) are special cases of equations (51)–(53). Note that $\{\tau\} = 1$ as for μ (§ 2.2).

From its definition (equation (52))

$$F'_{\tau ss'}(e, e') = F'^{*}_{\tau s's}(e', e) \tag{54}$$

so that if $I_{ee'}$ is real and symmetric (as in the non-resonant case)

$$c'_{\tau ss'} = c'^{*}_{\tau s's} \qquad \text{(NR)}. \tag{55}$$

This may be verified directly from equations (23), (29), (53) together with the 6*j* symbol symmetry

$$\begin{Bmatrix}\mu & 1 & 1\\ \tau^* & 1 & 1\end{Bmatrix}^*_{r's'sr} = \varepsilon_r^{\mu}\varepsilon_{r'}^{\mu}\varepsilon_s^{\tau}\varepsilon_{s'}^{\tau}\begin{Bmatrix}\mu & 1 & 1\\ \tau^* & 1 & 1\end{Bmatrix}_{rss'r'}. \tag{56}$$

Also from the definition of equation (52),

$$F'_{\tau ss'}(e, e') = \{1\,1\tau s\}\{1\,1\tau s'\}F'_{\tau ss'}(\tilde{e}, \tilde{e}'). \tag{57}$$

It follows that if we are dealing with linearly polarised light (LP), from equation (57) with $e = \tilde{e}$ etc,

$$\{1\,1\tau s\}\{1\,1\tau s'\} = 1 \qquad \text{(LP/CU, NR)}. \tag{58}$$

The selection rule of equation (58) is the analogue in this coupling of equation (23), and renders this coupling advantageous if only linearly polarised light is considered; one need consider only those cases in which both the sth and s'th occurrence of τ appear in either the symmetrised or antisymmetrised product $[1 \otimes 1]_{\pm}$. Again, if any particular symmetry of the intermediate state is dominant, this will select certain irreps τ as being of special importance.

6. Discussion

It is expected that the tables given here will prove useful in a wide variety of systems. Most molecules are taken to have non-degenerate ground states (Koningstein and Parameswaram 1976) in which case earlier tables (of McClain 1971) are adequate. However, even for orientationally averaged scatterers there are many applications where this is not true (e.g. all systems with Kramers degeneracy) and table 5 should permit a new appraisal of the coordination of lanthanide ions in solution, for example. Degeneracy of the ground electronic levels is possible for non-Kramers ions also, and Raman scattering is a suitable tool for its investigation. Table 3 should prove useful to workers in solid state spectroscopy, where the high symmetry of a substitutional site commonly introduces orbital degeneracy.

It is clear that the reciprocity condition of equation (17) may be generalised straightforwardly to higher-order photon processes. In particular, this gives a new selection rule for vibrational CARS (coherent anti-Stokes Raman scattering) in the non-resonant limit. We shall consider the consequences of this and similar rules elsewhere.

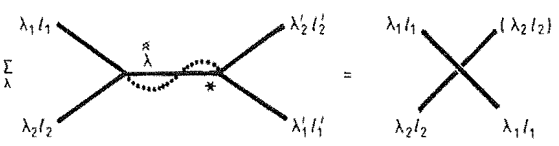
When this manuscript was finalised, we received a preprint of Barron and Nørby Svendsen (1980). These authors confirm the Child selection rules (equation (13)) using a related approach, namely considering the symmetries of effective operators. They emphasise the connection with Rayleigh scattering in degenerate systems, and extend their method to resonance scattering and to magneto-optical effects.

Acknowledgments

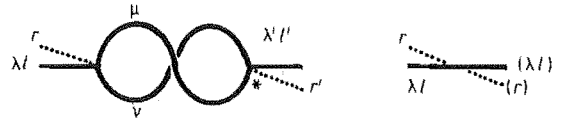
We are grateful to Dr R W G Syme, Professor B G Wybourne and Mr M F Reid for discussions. CDC is grateful to the New Zealand University Grants Committee for a Postgraduate Scholarship.

Appendix 1. Diagram approach to symmetry principles

Consider a symmetry group G(for §4, the full rotation group, for §3, the symmetry group of the scattering centre). The 3*jm* symbol will be represented as in Stedman (1975, 1976) by a vertex of degree 4, three legs representing the irrep labels, and the fourth the possibility of repetitions of one irrep in the Kronecker product of the other two. The 3*jm* symbols satisfy the orthogonality relations



(A1.1)

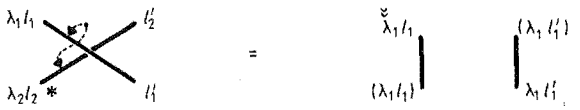


(A1.2)

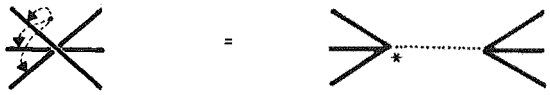
(fully labelled diagrams are given in the works cited). If 0 is the identity irrep of G, the triangle denotes a group operator O_g, and a broken line ending in a full circle an average over g, we have that

(A1.3)

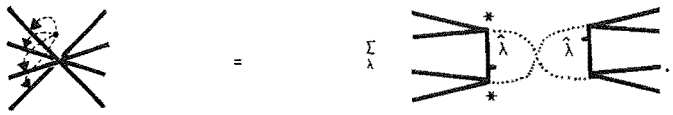
On combining equations (A1.1) and (A1.3), we may prove the following relations, the first of which is the great orthogonality theorem:



(A1.4)

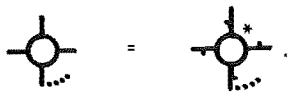


(A1.5)



(A1.6)

These results are particularly important when applied to a node of corresponding degree which is invariant, i.e. unaltered by application of an arbitrary group operation simultaneously to all legs. Then equation (A1.4) gives rise to JLV 2 (Schur's lemma) and equation (A1.5) to JLV 3 (Wigner–Eckart theorem) etc. The generalised Derome–Sharp lemma in diagram form states that a node may be complex-conjugated by a unitary transformation of all labels:



(A1.7)

When this holds for a physical quantity, a strong physical condition is implied; for the polarisation vector $\boldsymbol{e}$, the self-conjugacy condition is that of linearly polarised light (equation (25)), while for the transition amplitude $R^{kll'}_{\rho\sigma}(\Omega)$ or for the constants $f_{\mu\nu\tau}$ (equation (24)) or $c_{\mu\tau\tau'}$ (equation (32)), self-conjugacy is associated with time-reversal invariance of the contributing interactions. This follows essentially from equation (38) of Stedman and Butler (1980); the coefficient u^{κ}_{k} of a tensor operator (corresponding to the matrix element of the interaction Hamiltonian in the boson field) is self-conjugate (in all labels, including SO_3 parentage labels) if the interaction is time-reversal even. The phases associated with parentage conjugation ($ja\lambda \rightarrow ja^*\lambda^*$) will cancel in a quadratic such as $g_{\rho\rho'\sigma\sigma'} = \Sigma_{kll'} R^{kll'}_{\rho\rho'}(R^{kll'}_{\sigma\sigma'})^*$.

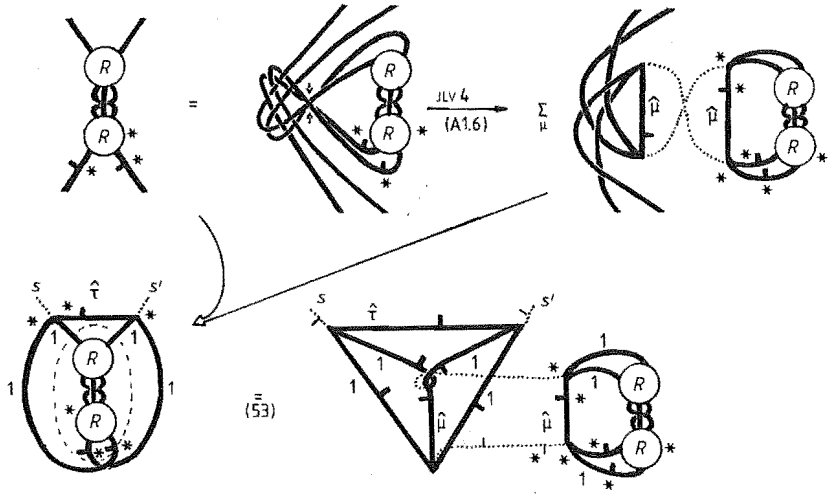


Figure A1. Proof of equation (53). The perspective used in the upper set of diagrams is to clarify the connections and does not denote entanglements.

Since $R^{ktl'}_{\rho\rho'}(\Omega)$ is left invariant (l, l' transform as ket labels) we assign the node R parity -1, and therefore the node e parity $+1$. A typical proof—that of equation (53)—is given in detail in figure A1.

Appendix 2.

The reducible $3jm$ symbol of equation (7) is defined by the basis transformations $\langle\rho\rho'|ja\lambda l\rangle$ of table A1 through the relation (using equation (46))

$$\lambda\begin{pmatrix}1 & 1 & \lambda\\ \rho & \rho' & l\end{pmatrix}^{r} = \langle\rho\rho'|r\lambda l\rangle \tag{A2.1}$$

with $r = ja$ and l generally specified by irrep labels in a maximal chain of subgroups. The interchange symmetry $\langle\rho\rho'|ja\lambda l\rangle = (-1)^{j}\langle\rho'\rho|ja\lambda l\rangle$ may be used to find the remaining off-diagonal terms.

The generalised Derome–Sharp lemma applied to this basis transformation yields

$$\langle\rho\rho'|ja\lambda l\rangle = \langle j'a'\lambda^{*}l^{*}|\rho\rho'\rangle\begin{pmatrix}\lambda\\ l\end{pmatrix}^{*} A^{*}_{ja,\,j'a'} \tag{A2.2}$$

where we use the basis of equation (46) and ignore $2jm$ symbols for the cartesian labels. By considering the connection with the transformation $\langle jm|ja\Lambda l\rangle$, together with the fact that SO_3 is simply reducible, it is readily shown that $A_{ja,j'a'}$ is zero if $j \neq j'$. We may define

$$A_{aa'} = \sum_{l\rho\rho'} \tilde{\lambda}\langle ja\lambda l|\rho\rho'\rangle\langle ja'\lambda^{*}l^{*}|\rho\rho'\rangle\begin{pmatrix}\lambda\\ l\end{pmatrix}^{*}. \tag{A2.3}$$

It is then readily verified that the transformations of table A1 are *not* consistent with the choice $A_{aa'} = \delta_{aa'}$. If (because of its complex representations) T is not used as a group in the chain defining the branching label a, we find $A_{aa'} = \pm\delta_{aa'}$, and we call the sign factor $A_{aa} = \varepsilon^{ja}_{\lambda} = \varepsilon'_{\lambda}$ elsewhere in this paper. It is listed in table A1. It is not possible to eliminate ε'_{λ} by redefining the phase of any ket or kets; equation (A2.3) is unchanged by any such

Table A1. Basis transformations $\langle \rho\rho' | ja\lambda l \rangle$ in several group–subgroup schemes. Columns are labelled by $|ja\lambda l\rangle$, where a and l are irrep labels in the chain, except for K $\downarrow$ D_3 where an additional (subscripted) label is required. The irrep label λ may be chosen as that of any group G in the chain. Given G, λ, the corresponding label for $r \equiv ja$ is simplified as $r = 0, 1, \ldots$ and listed below the label λ in the appropriate ket. An asterisk on r indicates that $\varepsilon_r^\lambda = -1$; otherwise $\varepsilon_r^\lambda = +1$.

SO_3–K–D_3–C_3

	$\|0000\rangle$ 000	$\|11\bar{0}0\rangle$ 002*	$\|1111\rangle$ 022	$\|111{-}1\rangle$ 02 2	$\|2200\rangle$ 011	$\|22_111\rangle$ 0 00	$\|22_011\rangle$ 0 11	$\|22_11{-}1\rangle$ 0 0 0	$\|22_01{-}1\rangle$ 0 1 1
xx	$1/\sqrt{3}$	—	—	—	$-1/\sqrt{6}$	$-\frac{1}{2}$	—	$-\frac{1}{2}$	—
yy	$1/\sqrt{3}$	—	—	—	$-1/\sqrt{6}$	$\frac{1}{2}$	—	$\frac{1}{2}$	—
zz	$1/\sqrt{3}$	—	—	—	$\sqrt{2}/\sqrt{3}$	—	—	—	—
xy	—	$i/\sqrt{2}$	—	—	—	$-\frac{1}{2}i$	—	$\frac{1}{2}i$	—
yz	—	—	$\frac{1}{2}i$	$-\frac{1}{2}i$	—	—	$\frac{1}{2}i$	—	$-\frac{1}{2}i$
zx	—	—	$\frac{1}{2}$	$\frac{1}{2}$	—	—	$-\frac{1}{2}$	—	$-\frac{1}{2}$

SO_3–O–D_4–C_4

	$\|0000\rangle$ 000	$\|11\bar{0}0\rangle$ 002*	$\|1111\rangle$ 011	$\|111{-}1\rangle$ 01 1	$\|2200\rangle$ 011	$\|2222\rangle$ 000	$\|2\tilde{1}\tilde{2}2\rangle$ 001*	$\|2\tilde{1}11\rangle$ 000	$\|2\tilde{1}1{-}1\rangle$ 00 0
xx	$1/\sqrt{3}$	—	—	—	$-1/\sqrt{6}$	$1/\sqrt{2}$	—	—	—
yy	$1/\sqrt{3}$	—	—	—	$-1/\sqrt{6}$	$-1/\sqrt{2}$	—	—	—
zz	$1/\sqrt{3}$	—	—	—	$\sqrt{2}/\sqrt{3}$	—	—	—	—
xy	—	$i/\sqrt{2}$	—	—	—	—	$i/\sqrt{2}$	—	—
yz	—	—	$\frac{1}{2}i$	$-\frac{1}{2}i$	—	—	—	$\frac{1}{2}i$	$-\frac{1}{2}i$
zx	—	—	$\frac{1}{2}$	$\frac{1}{2}$	—	—	—	$-\frac{1}{2}$	$-\frac{1}{2}$

SO_3–D_∞–D_6–C_6

	$\|0000\rangle$ 00	$\|1\bar{0}\bar{0}0\rangle$ 02*	$\|1111\rangle$ 11	$\|111{-}1\rangle$ 1 1	$\|2000\rangle$ 11	$\|2222\rangle$ 00	$\|222{-}2\rangle$ 0 0	$\|2111\rangle$ 00	$\|211{-}1\rangle$ 0 0
xx	$1/\sqrt{3}$	—	—	—	$1/\sqrt{6}$	$\frac{1}{2}$	$\frac{1}{2}$	—	—
yy	$1/\sqrt{3}$	—	—	—	$1/\sqrt{6}$	$-\frac{1}{2}$	$-\frac{1}{2}$	—	—
zz	$1/\sqrt{3}$	—	—	—	$-\sqrt{2}/\sqrt{3}$	—	—	—	—
xy	—	$i/\sqrt{2}$	—	—	—	$-\frac{1}{2}i$	$\frac{1}{2}i$	—	—
yz	—	—	$\frac{1}{2}i$	$-\frac{1}{2}i$	—	—	—	$-\frac{1}{2}i$	$\frac{1}{2}i$
zx	—	—	$\frac{1}{2}$	$\frac{1}{2}$	—	—	—	$\frac{1}{2}$	$\frac{1}{2}$

SO_3–O–T–D_2–C_2

	$\|00000\rangle$ 0	$\|111\bar{0}0\rangle$ 1	$\|11111\rangle$ 1	$\|111\tilde{1}1\rangle$ 1	$\|22200\rangle$ 0	$\|22{-}200\rangle$ 0	$\|2\tilde{1}1\bar{0}0\rangle$ 0*	$\|2\tilde{1}111\rangle$ 0*	$\|2\tilde{1}1\tilde{1}1\rangle$ 0*
xx	$1/\sqrt{3}$	—	—	—	$-1/\sqrt{12} + \frac{1}{2}i$	$-1/\sqrt{12} - \frac{1}{2}i$	—	—	—
yy	$1/\sqrt{3}$	—	—	—	$-1/\sqrt{12} - \frac{1}{2}i$	$-1/\sqrt{12} + \frac{1}{2}i$	—	—	—
zz	$1/\sqrt{3}$	—	—	—	$1/\sqrt{3}$	$1/\sqrt{3}$	—	—	—
xy	—	$i/\sqrt{2}$	—	—	—	—	$-1/\sqrt{2}$	—	—
yz	—	—	—	$-i/\sqrt{2}$	—	—	—	—	$1/\sqrt{2}$
zx	—	—	$1/\sqrt{2}$	—	—	—	—	$i/\sqrt{2}$	—

Table A1—continued
SO_3–O–D_4–D_2–C_2

	$\|00000\rangle$ 00	$\|11\bar{0}\bar{0}0\rangle$ 14*	$\|11111\rangle$ 12	$\|111\bar{1}1\rangle$ 13*	$\|22000\rangle$ 11	$\|22200\rangle$ 23	$\|2\bar{1}\bar{2}00\rangle$ 02*	$\|2\bar{1}111\rangle$ 00	$\|2\bar{1}1\bar{1}1\rangle$ 01*
xx	$1/\sqrt{3}$	—	—	—	$-1/\sqrt{6}$	$-1/\sqrt{2}$	—	—	—
yy	$1/\sqrt{3}$	—	—	—	$-1/\sqrt{6}$	$1/\sqrt{2}$	—	—	—
zz	$1/\sqrt{3}$	—	—	—	$\sqrt{2}/\sqrt{3}$	—	—	—	—
xy	—	$i/\sqrt{2}$	—	—	—	—	$i/\sqrt{2}$	—	—
yz	—	—	—	$-i/\sqrt{2}$	—	—	—	—	$-i/\sqrt{2}$
zx	—	—	$1/\sqrt{2}$	—	—	—	—	$-1/\sqrt{2}$	—

procedure. This contrasts with the situation for $3jm$ symbols, where quasi-ambivalence implies that the corresponding matrix $A_{aa'}$ is not required in the Derome–Sharp lemma (Butler 1975). Table A1 in fact uses the Butler (1981) tables together with the Fano–Racah contrastandard transformation of § 3.

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Irreducible analysis of Raman spectra for all crystal point groups

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Abstract. Techniques for the optimal and maximal extraction of information by Raman scattering experiments are investigated. All optical interactions are assumed to be electric dipole. For each crystal point group symmetry, a minimal set of choices of experimental arrangement (i.e. choice of polarisation vectors for incoming and outgoing light beams, scattering geometry etc.) is given, together with the transformations necessary to determine the irreducible parts of the spectrum in each of several bases. The more detailed tables are presented as a supplementary publication, SP . While valid for all crystal point groups, they are restricted to the case of time reversal invariant scattering interactions, and also to symmetric scatterers. The latter restriction includes systems which may have an antisymmetric part to the scattering amplitude, but in which the scattering intensity is unchanged by interchanging the incoming and outgoing polarisation vectors. Circular polarisation studies are necessary for a complete analysis of any system. However, the conventional 90° and 180° scattering geometries are adequate. Related symmetries of the Mueller matrix of the scatterer are also analysed.

Short title : Irreducible analysis of Raman spectra
INSPEC Classification: 78.30, 33.20F

1 Introduction

Much work has been done on the polarisation dependence of two-photon processes. The symmetries of the non-resonant phonon Raman tensor for non-degenerate electronic states have been tabulated by many authors (e.g. Loudon, 1964, McClain 1971, Cummins and Schoen 1972) and for degenerate electronic states by Churcher and Stedman (1981), hereafter referred to as I. In the field of two-photon absorption, several workers (e.g. Inoue and Toyozawa 1965, Bader and Gold 1968, Doni et al 1974) have already investigated the polarisation dependence of the intensity, although under more restrictive assumptions.

In general, we may write the intensity of scattered light as a sum over products of geometrical factors F_α and physical constants c_α :

$$I_{\underset{\sim}{e}\underset{\sim}{e}'}(\Omega) = \sum_{\alpha=1}^{N} F_\alpha(\underset{\sim}{e},\underset{\sim}{e}')\ c_\alpha(\Omega). \qquad (1)$$

Here, as in I, it is convenient to take $I_{\underset{\sim}{e}\underset{\sim}{e}'}$ in Raman theory as the probability of absorbing a photon of polarisation $\underset{\sim}{e}$ and emitting a photon of polarisation $\underset{\sim}{e}'^*$ (the asterisk was omitted in I). Our theory may be applied to two-photon absorption, with $I_{\underset{\sim}{e}\underset{\sim}{e}'}$ as the intensity of absorption of photons of polarisation $\underset{\sim}{e}$ and $\underset{\sim}{e}'$. Ω is the set of frequencies of incoming and outgoing light. The geometrical factors $F_\alpha(\underset{\sim}{e},\underset{\sim}{e}')$ are fixed for any point group symmetry G, and specify all possible dependences on experimental arrangement, i.e. polarisation choices, scattering geometry, etc. The physical constants $c_\alpha(\Omega)$ enshrine the physical, as opposed to purely geometrical, aspects of the scattering, and may be regarded as the set of irreducible spectra of the system.

The number of terms, N, in the summation of equation (1) will depend on the point group symmetry and on the physical assumptions made about the scatterer. In I we considered only symmetric and time reversal invariant scatterers, in which exchanging the polarisation vectors of incoming and outgoing beams had no effect on the scattering intensity. This still permitted an antisymmetric part to the scattering amplitude, and merely forbade its interference against the symmetric part and was valid for nonresonant phonon spectroscopy when the electronic states are degenerate, for example. The number of terms N^{++} in this case (given by the number of columns of table 3 of I) varies from 3 for full rotational symmetry through 4 for cubic symmetry, 8 for D_3 symmetry and 17 for C_2 symmetry to 27 for C_1 (i.e. no) symmetry.

In our general development, we shall assume electric dipole coupling of the photons to the system, but shall not assume either symmetric or time reversal invariant scatterers. Our development thus applies to near resonant Raman scattering for example, and also to magnetic field induced Raman optical activity (e.g. magnetic Raman CID)(Barron 1980, de Figuerido and Raab 1980), though the symmetry group must then be taken as that in the presence of the field. Chiral effects will be discussed more fully elsewhere.

In the case of full rotational symmetry, the three terms correspond to the scalar, antisymmetric and symmetric traceless scattering tensor components (Placzek 1962), as labelled by the irrreducible representations (irreps) j=0, 1, 2 respectively of the rotation group. The associated geometrical factors $F_j(\underset{\sim}{e},\underset{\sim}{e}')$ are given in tables 4, 6 of I for example. Three measurements of the Raman spectrum of an orientationally averaged system suffice to determine its scattering properties

for any experimental arrangement, provided only that they are geometrically independent, in activating linearly independent proportions of the three irreducible components (j=0, 1, 2).

In this paper we determine a set of N geometrically independent experimental arrangements, and derive tables of transformation coefficients from experimental spectra to irreducible spectra. We learn as much as we can learn about the Raman scattering properties of a system when we have determined the N irreducible spectra $\{c_\alpha(\Omega)\}$. This in turn requires the measurement of N geometrically independent experimental spectra $\{I_\beta(\Omega)\}$, $\beta = 1, 2, \ldots, N$, where each β implies a choice of polarisation vectors $\underset{\sim}{e}_\beta$, $\underset{\sim}{e}_\beta'$. The geometrical independence of these measurements means that the geometrical factors of equation (1), regarded as a matrix $F_{\beta\alpha}$, will be nonsingular, and permits the inversion of the equation :

$$c_\alpha(\Omega) = \Sigma_\beta F^{-1}_{\alpha\beta} I_\beta(\Omega) \qquad (2)$$

We list the matrices $F^{-1}_{\alpha\beta}$ of equation (2) for all point groups in the supplementary publication (cf §3). Several choices of basis $\{\alpha\}$ may be used, and these are discussed in §2. Fröhlich et al (1970) and Bayer and Schaak (1970) have given a related analysis for the case of two-photon spectroscopy with $G = O_h$ (and thus N = 4); our generalisation fills the gap in such treatments noted, for example, by Worlock (1972) in his review.

The polarisation states of the incoming and outgoing light beams may be parametrised by the four independent and orthogonal components of the Stokes vector (Shurcliff 1962); the action of the scatterer is that of a 4 x 4 matrix transformation

of this scattering (Mueller) matrix in §4 and in particular consider the effects of such discrete symmetries as parity and time reversal as well as the point group symmetry of the scatterer in limiting the form of the Mueller matrix. We compare our results with those of other authors for the symmetries of the scattering matrix (Borcherds and Alfrey 1975, de Figueiredo and Raab 1980, Graham 1980).

2 Bases for the irreducible expansion and their dimension

2.1 Choice of experimental arrangements

In considering the fundamental scattering mechanisms, we shall assume the photons couple through the electric dipole interaction (thus ignoring natural optical activity and like effects) and shall distinguish three cases: an otherwise general interaction; a time reversal invariant (TRI) interaction; and a symmetric TRI interaction. Examples of these three cases are, respectively: Raman optical activity induced by external magnetic fields; electronic and/or resonance Raman effect; non-resonant phonon Raman effect. The corresponding number of terms in equation (1) will be written N, N^+, N^{++} respectively. Note that a symmetric scatterer lacking TRI would require $N_s = N^+$ terms; this follows from table 2. In general (§2.3)

$$N = 3N^+ - 2N^{++} \qquad (3)$$

When no point group symmetry is assumed, N = 81, N^+ = 45, and N^{++} = 27. These numbers are greatly reduced in a given point group symmetry (and are listed in table 2). First we consider the general case.

A geometrically independent set of N experimental arrangements may be chosen in an infinite number of ways. A standard choice may be made by choosing just those polarisation vectors fundamental to the definition of Stokes parameters in a cartesian basis. We thus consider only 9 types of polarisation vector $\underset{\sim}{e}$ or $\underset{\sim}{e}'$; light linearly polarised along a cartesian axis; light polarised at 45° to two axes; circularly polarised light propagating along each axis. These give 81 geometrically independent combinations in the general case.

In a TRI scatterer, and within our assumption of E1 coupling, Raman CID is forbidden; the preferred alteration of photon angular momentum is odd under time inversion. In this case we may ignore experimental arrangements which mix linear and circular polarisation choices, as the associated intensities are not independent of those in the arrangements we retain. (Note that within the E1 coupling assumption, parity or reflection symmetry considerations cannot forbid Raman CID effects except in special cases.) This leaves 45 arrangements. Finally, symmetric scatterers do not distinguish a choice $A_\beta B_\beta$ from the reverse $B_\beta A_\beta$; this leaves 27 cases. These choices are summarised in table 1.

Consider for example the case of symmetric TRI scatterers. Table 1 lists the 27 experimental arrangements of which 21 involve only linearly polarised light, and 6 only circularly polarised light. An overlapping set of 6 arrangements cannot be determined in 180° geometry, but can in 90° geometry. Another 6 arrangements cannot be determined in 90° geometry but can in 180° geometry. In general, then, both geometries are needed. Point group symmetry considerations will reduce the number of geometrically independent spectra of table 1, and may therefore eliminate the need for certain geometries (§3). However, this will not eliminate the need for circular

polarisation studies; we show that at least 6 experimental arrangements must involve circularly polarised light (§2.3).

2.2 Choices of basis

The set of N labels $\{\alpha\}$ required in equation (1) may be chosen in a variety of ways. Since each has its merits, we describe several at this stage. When using the tables, the reader will naturally choose whichever best suits the application. In the main paper we shall concentrate on the spherical basis.

In each choice it is useful to define a symmetrized geometrical factor $F_\alpha^{\eta\epsilon}(\underset{\sim}{e}, \underset{\sim}{e}')$ with its associated physical constant $c_\alpha^{\eta\epsilon}(\Omega)$ by

$$I_{\underset{\sim}{e}\underset{\sim}{e}'}(\Omega) = \Sigma_{\alpha\eta\epsilon} F_\alpha^{\eta\epsilon}(\underset{\sim}{e}, \underset{\sim}{e}')\, c_\alpha^{\eta\epsilon}(\Omega) \qquad (4)$$

$$F_\alpha^{\eta\epsilon}(\underset{\sim}{e}, \underset{\sim}{e}') = \eta\, F_\alpha^{\eta\epsilon}(\tilde{\underset{\sim}{e}}, \tilde{\underset{\sim}{e}}') \qquad (5)$$

$$= \epsilon\, F_\alpha^{\eta\epsilon}(\underset{\sim}{e}', \underset{\sim}{e}) \qquad (6)$$

where the conjugate polarisation vector $\tilde{\underset{\sim}{e}}$ reduces to $\underset{\sim}{e}^*$ in a cartesian basis, and represents light of opposite circular polarisation content. The restrictions $\eta = 1$, $\epsilon = 1$ correspond to TRI and symmetric scatterers respectively.

Cartesian basis

The standard tables of Raman scattering amplitudes (Loudon 1964) are traditionally written in a cartesian basis. Some components are chosen as the set of primitive constants, and the remainder expressed in terms of them using the symmetry constraints.

A similar representation may be given for the intensities, which are quartic in the polarisation vectors. Equation (1) becomes

$$I_{\underset{\sim}{e}\underset{\sim}{e}'}(\Omega) = \Sigma_{\rho\rho'\sigma\sigma'} F_{\rho\rho'\sigma\sigma'}(\underset{\sim}{e}, \underset{\sim}{e}')\, c_{\rho\rho'\sigma\sigma'}(\Omega) \qquad (7)$$

If the summation is over all 81 sets of values of $\rho,\rho',\sigma,\sigma' = x,y,z$, $F_{\rho\rho'\sigma\sigma'}(\underset{\sim}{e}, \underset{\sim}{e}')$ may be identified as the quartic $e_\rho e'_{\rho'} e^*_\sigma e'^*_{\sigma'}$. We define the symmetrised geometrical factors by

$$[\underset{\sim}{e}\underset{\sim}{e}']^{\eta\epsilon}_{\rho\rho'\sigma\sigma'} = \theta_\eta [e_\rho e'_{\rho'} e^*_\sigma e'^*_{\sigma'} + \epsilon e_{\rho'} e'_\rho e^*_{\sigma'} e'^*_\sigma + \eta(e_\sigma e'_{\sigma'} e^*_\rho e'^*_{\rho'} + \epsilon e_{\sigma'} e'_\sigma e^*_{\rho'} e'^*_\rho)]/k \qquad (8)$$

where $k = 4$ if the cartesian labels ρ, ρ', σ, σ' are all equal (note that only $\eta = \epsilon = 1$ survive in this case), $k = 2\sqrt{2}$ if the cartesian labels are equal in pairs, and $k=2$ otherwise. $\theta_\eta = 1(i)$ as $\eta = 1\ (-1)$. The intensity becomes

$$I_{\underset{\sim}{e}\underset{\sim}{e}'}(\Omega) = \Sigma_{(\rho\rho'\sigma\sigma')\eta\epsilon} [\underset{\sim}{e}\,\underset{\sim}{e}']^{\eta\epsilon}_{\rho\rho'\sigma\sigma'} c^{\eta\epsilon}_{\rho\rho'\sigma\sigma'}(\Omega) \qquad (9)$$

where the sum is over the 27 sets of labels given in table 3 of I, for example. Point group symmetry reduces this number. The independent linear combinations $F^{\eta\epsilon}_{\rho\rho'\sigma\sigma'}(\underset{\sim}{e}, \underset{\sim}{e}')$ of the $[\underset{\sim}{e}\,\underset{\sim}{e}']^{\eta\epsilon}_{\rho\rho'\sigma\sigma'}$ are given in the supplementary publication. The factors $[\underset{\sim}{e}\,\underset{\sim}{e}']^{++}_{\rho\rho'\sigma\sigma'}$ appropriate to each choice of experimental arrangement in table 1 are also given in the supplementary publication.

The cartesian basis is familiar also in other crystal tensor theory. For example, the elastic constant tensor is also quartic, and has the symmetries of $[\underset{\sim}{e}\,\underset{\sim}{e}']^{++}_{\rho\rho'\sigma\sigma'}$. However it enjoys the further symmetry

$$c_{\rho\rho'\sigma\sigma'} = c_{\rho\rho'\sigma'\sigma} \qquad (10)$$

which allows Voigt notation and other simplifications. These are inapplicable here.

A very useful representation is that in terms of spherical tensor labels. Two polarisation vectors in the quartic $e_\rho e'_{\rho'} e^*_\sigma e'^*_{\sigma'}$ are coupled to give tensor components of angular momentum $j_1 = 0, 1, 2$. The remaining two are coupled likewise to angular momentum j_2. Finally, j_1 and j_2 are coupled to angular momentum j and component m. With the modifications detailed below, the set of labels $j_1 j_2 j m$ may be used in lieu of cartesian or point group labels. The connection with the cartesian label choice is that a cartesian tensor may be decomposed into components of definite spherical symmetry (Jerphagnon et al 1978). In the standard coupling detailed below, the connection with the point group basis choice is that the r-th occurrence of μ is contained in j_1, and r'-th occurrence in j_2.

In the standard choice of coupling made in I, we first couple an incoming with an outgoing polarisation vector, to form the intermediate tensor of symmetry j_1. Thus we consider a geometrical factor

$$F_{j_1 j_2 j m}(\underset{\sim}{e},\underset{\sim}{e}') = [[\underset{\sim}{e}\underset{\sim}{e}']^{j_1}[\tilde{\underset{\sim}{e}}\tilde{\underset{\sim}{e}}']^{j_2}]^{j}_{m} \qquad (11)$$

where the square brackets denote irreducible coupling within We perform the symmetrisations of equation (4) and also combine terms with opposite sign of m, as in crystal field theory (symmetric and antisymmetric combinations labelled by $\theta = \pm 1$), thus arriving at geometric factors $F^{\eta\epsilon}_{j_1 j_2 j m\theta}(\underset{\sim}{e}, \underset{\sim}{e}')$. Details of these symmetrisations are given in the supplementary publication, together with the unitary transformation $T^{\eta\epsilon\, j_1 j_2 j m\theta}_{\rho\rho'\sigma\sigma'}$ connecting these geometrical factors with the symmetrised geometrical factors in the cartesian basis. The symmetries of this unitary transformation give the following restrictions in the standard coupling of equation (11):

For symmetric TRI scatterers ($\eta = \epsilon = 1$):

$$j_1 + j_2 = 2n \qquad (12)$$

$$j = 2n' \qquad (13)$$

where n, n' are integers. For TRI, but not necessarily symmetric, scatterers ($\eta = 1$):

$$j_1 + j_2 + j = 2n \qquad (14)$$

In the alternative coupling, discussed in §5 of I, we associate j_1 with the coupling of the polarisation vectors of the incoming beam, and so define new geometrical factors $F'_{j_1 j_2 j m}(\underset{\sim}{e},\underset{\sim}{e}') = [(\underset{\sim}{e}\tilde{\underset{\sim}{e}})^{j_1}[\underset{\sim}{e}'\tilde{\underset{\sim}{e}}']^{j_2}]^{j}_{m}$. Symmetrising as above we would have new real geometrical factors obeying the constraints of equations (12),(13) for symmetric TRI scatterers. However, for TRI scatterers, equation (14) is replaced by

$$j_1 + j_2 = 2n. \qquad (15)$$

Invariance under the point group G implies that we should always consider certain linear combinations of terms with the same j labels but different m labels, so as to construct a basis function of the identify irrep 0 of G. This will always involve the symmetrisation of +m with -m ($\theta = \pm 1$) , and this step is normally sufficient. (A further linear combination is required in the case j = 4 in the cubic groups, where symmetry operations mix m = 0 and $m\theta$ = 4+ terms). Tables of point group symmetrised functions are given in Butler (1981) for all point groups. The implicit choice of crystal axes is discussed by Reid and Butler (1980).

For the case of symmetric TRI scatterers, the restrictions detailed above for the labels j and m are identical to those on the crystal field parameter B^m_j for d shell electronic states.

Point Group basis

One fundamental choice of basis is that used in I, viz. the irreducible labels of the point group in question. We write $\{\alpha\} \equiv \{\mu rr'\}$; μ is an irrep of the point group G, and r,r' enumerate the repetitions of μ in the second rank tensor representation $\underset{\sim}{1}^- \times \underset{\sim}{1}^-$ of G ($\underset{\sim}{1}$ being the vector representation and the minus specifying the parity of the electronic operator in the interaction).

Again, this basis requires symmetrisation and restriction of the terms in various point groups. The details are given in the supplementary publication.

2.3 Enumeration of terms; physical consequences

We list in table 2 the possible terms $j_1 j_2 jm\theta^{\eta\epsilon}$ allowed under the foregoing rules for each point group, for each coupling choice and physical restriction (to symmetric and/or TRI scatterers) of interest, using the spherical basis.

The transformations between bases are given in diagram form in figure 1 and in detail in the supplementary publication.

It is now readily seen from table 2 that circular polarisation studies are essential for a complete investigation of a system of any point group symmetry. Consider the alternative coupling, in which $j_1 = 1$ and $j_2 = 1$ correspond to a coupling $[\underset{\sim}{e}\underset{\sim}{\tilde{e}}]^1$, and $[\underset{\sim}{e}'\underset{\sim}{\tilde{e}}']^1$ respectively, i.e. to $\underset{\sim}{e} \times \underset{\sim}{e}^*$ and $\underset{\sim}{e}' \times \underset{\sim}{e}'^*$ respectively. Such terms ($j_1 = j_2 = 1$) are required in every symmetry even for symmetric TRI scatterers. This is a consequence of the occurrence of the universally invariant term $j = 0$ in $1 \otimes 1$. However, the above vector products vanish unless both polarisation vectors are complex, and thus correspond to light beams with a circularly polarised component. Likewise, terms with both j_1 and j_2 even may be associated with experiments involving two linearly polarised beams, and terms with $j_1 + j_2$ being odd may be associated with experiments involving one linearly and one circularly polarised beam.

In the groups $R_3(SO_3)$, K, O, O_h, T_d, it is not possible to find invariant sets of labels unless $\eta = \epsilon = 1$ (table 2). It follows that scatterers with this high degree of symmetry are always apparently symmetric and time reversal invariant in their Raman scattering properties, whether or not the basic scattering mechanisms obey these constraints. Optical activity could not be seen in such a system, despite the fact that O is a chiral point group; this reflects our limitations to E1 photon interaction.

3 Analysis of experimental data

In order to determine the Raman scattering properties of a system of known symmetry, one need choose only N experimental arrangements from those listed in table 1, provided the resulting choices are geometrically independent. We write this set of N primitive arrangements as $(A_\beta B_\beta,\ \beta = 1, 2, \ldots N)$ and denote the corresponding experimental spectra in the same notation (e.g. $I_{(100)(100)}(\Omega) = XX$, etc.). The remaining experimental arrangements are redundant, in that linear relations connect the corresponding spectra to the N primitive spectra. We use the tables of I to determine these relations for the case of symmetric TRI scattering ($N \to N^{++}$); they are given in table 3. For most of the remainder of this paper, we shall limit our detailed considerations to symmetric TRI scatterers, where the matrices are much smaller than in the general case.

One could in principle use the relations of table 3 to check the assumed symmetry of the scattering process, if (as for nonresonant phonon Raman spectroscopy) it were known to be symmetric and TRI. (There would of course be practical problems in the relative normalisation of spectra taken under differing experimental conditions). Groups listed together in table 3 may not be distinguished by this method; for example, T and O give different constraints on the geometrical dependence of the Raman spectrum only if antisymmetric or time reversal odd effects are considered.

The relations of table 3 may render some types of experimental arrangement unnecessary. As proved in §2.3, circular polarisation studies will always be necessary for a full analysis. However, in all symmetries higher than C_2, the arrangements GH, HI, GI are never primitive, so that circular polarisation measurements need only be carried out in 180° scattering geometry. In addition, for all groups except C_2, C_3 (and those indistinguishable from them), it is possible to investigate the system using a 180° scattering geometry for every measurement. It is not possible to avoid 180° scattering geometry for a complete analysis of any group.

Given the N^{++} primitive spectra $\{A_\beta B_\beta\}$, we may find the irreducible spectra $\{c_\alpha(\Omega)\}$ by a matrix transformation (equation 2). This may prove a more useful characterisation of the Raman scattering properties of the system, in that definite physical scattering mechanisms may contribute preferentially to certain irreducible spectra, so that their characteristic effects are more readily determined. This could be particularly helpful in disentangling contributions to a broad Raman spectral feature, arising from overlapping lines or second order effects.

The choice of basis is dictated by personal taste, although consideration of the symmetry of the excitation responsible for the Raman scattering may make some bases more convenient than the others. The scattering mechanism may have definite symmetry under either the point group G or in some higher group $\hat{G}$; for example in phonon spectroscopy $\hat{G}$ would correspond to the $\underset{\sim}{k} = 0$ factor group of the crystal. Such parentage considerations may restrict the choice of the branching multiplicity labels r, r' used in the point group basis, which are themselves usually parentage labels; this would favour the use of the point group basis. If the

scattering mechanism preserved some features of the higher symmetry, these might make the correspondingspectra $c_{j_1 j_2 jm}(\Omega)$ of greater importance than those excited only in the lower symmetry, etc.

The transformation matrices $F_{\beta,\mu rr'}$, $F^{-1}_{\mu rr',\beta}$ for the point group basis are listed in the supplementary publication, together with the transformations to the cartesian basis, the restrictions imposed by point group symmetry on the cartesian labels, and the transformation matrix $F_{\beta,j_1 j_2 jm\theta}$, for the spherical basis. The inverse matrix $F^{-1}{}_{j_1 j_2 jm\theta,\beta}$, is arguably the most important for practical applications and is relatively compact; we include it in the body of the paper (table 4).

As a simple example of the application of these tables we consider the case G = 0. Table 2 gives the four non-vanishing spectrum labels $j_1 j_2 jm\theta$ for the octahedral group; table 4, together with the relationships in table 3, then relate these to the experimental spectra as follows :

$$c_{0000} = XX + 2DD - 2HH \quad (16)$$

$$c_{1100} = \sqrt{3}\,(XX + 2XY - DD - HH) \quad (17)$$

$$c_{2200} = (1/\sqrt{5})(-XX + DD + 5HH) \quad (18)$$

$$c_{224c} = (12/\sqrt{30})(XX - DD) \quad (19)$$

Using the material in the supplementary paper, we may derive similar expressions for the other choices of basis, and the transformations, e.g. between the spherical and point group bases $c_{j_1 j_2 jm} \leftrightarrow c_{\mu rr'}$:

$$c_{0000} = c_{000} \quad (20)$$

$$c_{1100} = c_{100} \quad (21)$$

$$c_{2200} = (1/\sqrt{5})(\sqrt{2}c_{200} + \sqrt{3}c_{\tilde{1}00})$$

$$c_{224c} = (1/\sqrt{15})(\sqrt{3}c_{200} - \sqrt{2}c_{\tilde{1}00}) \quad (22)$$

where $\mu = 0, 1, 2, \tilde{1}$ label $\Gamma_1, \Gamma_4, \Gamma_3, \Gamma_5$ respectively.

Note that in equations (16)-(19), the asymmetric spectrum XY appears only in c_{1100} (i.e. c_{100} in the point group basis). This term corresponds to an antisymmetric component of the amplitude ($j = 1 \in [1 \times 1]_-$, $\Gamma_4 \in [\Gamma_4 \times \Gamma_4]_-$), and would not arise in the discussion of non-resonant phonon spectra in nondegenerate system, or two-photon spectroscopy with equal photon energies (Fröhlich et al 1970). The above relations amount to the inverse of a submatrix of table 1 of Frohlich et al (1970); our XX is their $S_1^{(1)}$, our DD their $S_2^{(1)}$, etc., and our $c_{\mu rr'}$ is apart from normalisation their λ_i. In this manner one may determine the four irreducible parts of the spectrum from four experiments.

If we had used the alternative coupling of §2.2, equations (16)-(19) would have included the spectrum HH only in the expression for c_{1100} (or equivalently c'_{100} in the point group basis), since in this case HH represents the essential measurement with circularly polarised light.

4 Mueller matrix of the scatterer

An alternative approach to the problem of determining symmetry-induced restrictions on Raman scattering is that of using Mueller matrices and Stokes vectors to describe the scatterer and the light beams (Shurcliff 1962, McMaster 1961, Collett 1970). This has been applied by Borcherds and Alfrey (1975) and Graham (1980) for example in Raman scattering theory.

The Stokes parameters may be defined by

$$S^\mu = (\underset{\sim}{D}\underset{\sim}{e})^* \cdot \underset{\sim}{g}^\mu \cdot (\underset{\sim}{D}\underset{\sim}{e}) \quad . \tag{23}$$

$(S^\mu) = (I, M, C, S)$ is a 4-tuple ($\mu = 0, 1, 2, 3$) with I representing the intensity, and M, C, S the tendency for the light to be horizontally, diagonally and circularly polarised respectively. $\underset{\sim}{g}^\mu$ represents the four 3 x 3 matrices

$$\tfrac{1}{2}\begin{pmatrix}1&0&0\\0&1&0\\0&0&0\end{pmatrix}\ ,\ \tfrac{1}{2}\begin{pmatrix}1&0&0\\0&-1&0\\0&0&0\end{pmatrix}\ ,\ \tfrac{1}{2}\begin{pmatrix}0&1&0\\1&0&0\\0&0&0\end{pmatrix}\ ,\ \tfrac{1}{2}\begin{pmatrix}0&-i&0\\i&0&0\\0&0&0\end{pmatrix}$$

Of these components, only the 2 x 2 block at the top left of each is relevant (i.e. the Pauli matrices $(\sigma)_{ab}$), since the orthogonal matrix $\underset{\sim}{D}$ is chosen to rotate the polarisation vector into a basis with the propagation direction in the +z direction ($(\underset{\sim}{D}\underset{\sim}{e})_z = 0$).

The probability of scattering a photon of polarisation vector $\underset{\sim}{e}'$ off a Raman scatterer which is subjected to a light beam of polarisation $\underset{\sim}{e}$ and whose amplitude for scattering is $\underset{\sim}{R}^\xi$ (with ξ enumerating all possible initial and final states of the scatterer) is proportional in E1 coupling to

$$P(\underset{\sim}{e} \to \underset{\sim}{e}') = \Sigma_\xi \left| \underset{\sim}{e} \cdot \underset{\sim}{R}^\xi \cdot \underset{\sim}{e}'^* \right|^2 \tag{24}$$

We may write this in terms of the Stokes parameters S^μ , S'^μ appropriate for $\underset{\sim}{e}$, $\underset{\sim}{e}'$ by writing the general bilinear combination as

$$e_\rho e^*_\sigma = \Sigma_\mu A^\mu_{\rho\sigma} S^\mu \tag{25}$$

where from the above definitions (using $\Sigma_\mu \sigma^\mu_{ab}\sigma^\mu_{cd} = \tfrac{1}{2}\delta_{ad}\delta_{bc}$)

$$\underset{\sim}{A}^\mu = 2\underset{\sim}{D}^T \cdot \underset{\sim}{g}^\mu \cdot \underset{\sim}{D} \tag{26}$$

Substituting into equation (24), we find

$$P(\underset{\sim}{e} \to \underset{\sim}{e}') = \Sigma_{\mu\nu} S^\mu M_{\mu\nu} S'^\nu \tag{27}$$

with

$$M_{\mu\nu} \equiv \Sigma_{\rho\rho'\sigma\sigma'} A^\mu_{\rho\sigma} A'^\nu_{\rho'\sigma'}{}^* T_{\rho\rho'\sigma\sigma'} \tag{28}$$

$$T_{\rho\rho'\sigma\sigma'} \equiv \Sigma_\xi R^\xi_{\rho\rho'} \left(R^\xi_{\sigma\sigma'}\right)^* \tag{29}$$

The probability of finding a photon characterised by a Stokes vector P_1 in a beam characterised by a Stokes vector P_2 is proportional to $\Sigma_\mu P^\mu_1 P^\mu_2$. Hence, equating P_1 and $P(\underset{\sim}{e} \to \underset{\sim}{e}')$, the scattered beam is characterised by the Stokes vector

$$P^\mu = \Sigma_\nu M_{\mu\nu} S^\nu \tag{30}$$

and $M_{\mu\nu}$ is thus the Mueller matrix of the scatterer.

We look for symmetry restrictions on the form of the Mueller matrix. These depend on the scattering geometry and axis choices (which enter the definitions of $\underset{\sim}{D}$ and $\underset{\sim}{D}'$).

From §2.1, we need consider only 90° or 180° scattering. The orientations of table 1 include 18 cases (those involving Z, D, E, G, H) in which $\underset{\sim}{D}$ and/or $\underset{\sim}{D}'$ must be nontrivial, since e_z (or e_z') $\neq 0$. However, even in these cases, only an axis permutation (D: $x \rightleftharpoons y \rightleftharpoons z$ or $x \rightleftharpoons z$ etc.) is needed to make $e_z = 0$. In all cases then we may write

$$A^{\mu}_{\rho\sigma} = \sigma^{\mu}_{D(\rho)D(\sigma)} \tag{31}$$

where $D(\rho)$ denotes the relabelling of axes. Equation (28) becomes

$$M_{\mu\nu} = 4\Sigma_{\rho\rho'\sigma\sigma'}\sigma^{\mu}_{D(\rho)D(\sigma)}\sigma^{\nu}_{D'(\rho')D'(\sigma')}{}^{*}T_{\rho\rho'\sigma\sigma'} \tag{32}$$

Note that $\underset{\approx}{\sigma}^{\mu}$ and thus $\underset{\approx}{A}^{\mu}$ are hermitian and that the Stokes parameters S^{μ} and the Mueller matrix elements $M_{\mu\nu}$ are real.

Time reversal invariance constrains $T_{\rho\rho'\sigma\sigma'}$ to be real (cf. §2.2 for a discussion of the related quantity $c_{\rho\rho'\sigma\sigma'}$). Since $\left(\underset{\approx}{\sigma}^{\mu}\right)^{*} = c_{\mu}\underset{\approx}{\sigma}^{\mu}$, with $(c_{\mu}) = (+, +, +, -)$ equation (32) gives $M^{*}_{\mu\nu} = c_{\mu}c_{\nu}M_{\mu\nu}$. Since $M_{\mu\nu}$ is real, the elements M_{is}, M_{si} must vanish in all systems. Thus our assumption of time reversal invariance forbids generation of a circularly polarised component from linearly polarised light, as seen in §2.

The assumption of a symmetric scatterer gives in equation (32) that

$$M_{\mu\nu}\left(\underset{\approx}{D}, \underset{\approx}{D}'\right) = M_{\nu\mu}\left(\underset{\approx}{D}', \underset{\approx}{D}\right). \tag{33}$$

In forward scattering, we may take $\underset{\approx}{D} = \underset{\approx}{D}'$ and the Mueller matrix is symmetric. In 180° scattering, the propagation vectors are reversed. Taking $\underset{\approx}{D}\underset{\approx}{D}'^{T} = \underset{\approx}{P} = \mathrm{diag}(-1, 1, -1)$ gives

$$\sigma^{\mu}_{P(\rho)P(\sigma)} = \varepsilon_{\mu}\sigma^{\mu}_{\rho\sigma} \tag{34}$$

$$\sigma^{\mu}_{D(\rho)D(\sigma)}\sigma^{\nu}_{D'(\rho')D'(\sigma')}{}^{*} = \varepsilon_{\mu}\varepsilon_{\nu}\sigma^{\mu}_{D'(\rho)D'(\sigma)}\sigma^{\nu}_{D(\rho')D(\sigma')}{}^{*}$$

where $\varepsilon_{\mu} = \pm 1$ as $\mu = 0, 1$ or $2, 3$ respectively. Together with equation (32), this gives that $M_{\mu\nu} = \varepsilon_{\mu}\varepsilon_{\nu}M_{\nu\mu}$. With this choice of relative axes for incoming and outgoing light, then, and for 180° scattering by symmetric scatterers

$$\underset{\approx}{M} = \begin{pmatrix} M_{00} & M_{01} & M_{02} & \cdot \\ M_{01} & M_{11} & M_{12} & \cdot \\ -M_{02} & -M_{12} & M_{22} & \cdot \\ \cdot & \cdot & \cdot & M_{33} \end{pmatrix} \tag{35}$$

In 90° scattering, say in the yz plane (k//y and k'//z for definiteness), we may choose beam axes so that

$$\underset{\approx}{P} = \underset{\approx}{D}\underset{\approx}{D}'^{T} = \begin{pmatrix} 1 & \cdot & \cdot \\ \cdot & \cdot & 1 \\ \cdot & -1 & \cdot \end{pmatrix} \tag{36}$$

In this case $\sigma^{\mu}_{P(\rho)P(\sigma)}$ is more complicated; no two matrices $\underset{\approx}{\sigma}^{\mu}$ have simple transformation properties under P, and no simple symmetry can be claimed for the Mueller matrix, apart from the time reversal symmetry discussed above.

Further simplifications may be achieved by specialising to some particular symmetry group G. We first detail a simple example, following Borcherds and Alfrey (1975). Suppose that the system has as a symmetry operation $\underset{\approx}{R}$ a C_2 rotation about an axis perpendicular to the plane of scattering. In this case $T_{R(\rho)R(\rho')R(\sigma)R(\sigma')} = T_{\rho\rho'\sigma\sigma'}$. Taking the plane of scattering to include the z axis, and the C_2 axis to be the

x or y axis, $\underset{\sim}{R} = \mathrm{diag}(\pm 1, \mp 1, -1)$, $\sigma^{\mu}_{R(\rho)R(\sigma)} = \varepsilon^{\mu}\sigma^{\mu}_{\rho\sigma}$ so that from equation (32)

$$M_{\mu\nu} = \Sigma_{\rho\rho'\sigma\sigma'} \quad \sigma^{\mu}_{DR(\rho)DR(\sigma)}\sigma^{\nu}_{D'R(\rho')D'R(\sigma')^{*}}T_{\rho\rho'\sigma\sigma'} = \varepsilon^{\mu}\varepsilon^{\nu}M_{\mu\nu} \qquad (37)$$

Hence all matrix elements with $\mu = 0, 1$ and $\nu = 2, 3$ vanish and the Stokes parameters C, S will never be generated from a beam which does not contain them by Raman scattering off such a system. (The relevant groups are D_n, O, T and groups containing these).

In this connection we comment on another conclusion of Borcherd and Alfrey (1975), who state that it is possible to determine whether or not a crystal has a centre of symmetry, by using a scattering geometry of low symmetry. By this they still mean 90° scattering, but with the crystal rotated at an oblique angle so that neither $\underset{\sim}{k}$ nor $\underset{\sim}{k}'$ coincide with a cartesian axis of the system. They indicate that this then permits the generation of Stokes parameters C, S from a beam that may not contain them, and the consequent proof that a centre of symmetry does not exist. These conclusions conflict both with the proof in §2 that all properties of a scatterer may be determined by measurements with the scattering geometry chosen so that $\underset{\sim}{k}$, $\underset{\sim}{k}'$ are along the cartesian axes of the system, and with the proof in this section that the parameter S can never be generated from a beam which does not contain it by Raman scattering.

The first conflict is due to the fact that Borcherds and Alfrey (1975) limited themselves to a linearly polarised primary beam with both C and S non-zero. The full analysis of §2 while only requiring simple geometries does require primary beams with C or S non-zero. On the second point, our analysis supercedes and corrects that of Borcherds and Alfrey. It is based on time reversal invariance, independent of point group symmetry. We find that a crystal with a centre of symmetry (say $G = C_{6h}$) may generate a C parameter when the scattering plane is not perpendicular to the 2-fold axis; conversely, the lack of a C parameter need not require a centre of symmetry, but merely a 2-fold axis perpendicular to the scattering plane. In fact, within our restriction to E1 coupling, space inversion does not give a simple symmetry of the Mueller matrix; the matrices $\underset{\sim}{\sigma}^{\mu}$ are scalars. de Figueiredo and Raab (1980) and Graham (1980) combine space inversion with a rotation (thus a reflection) to describe two Stokes parameters as pseudoscalar, and obtain a simple symmetry for the Mueller matrix, analogous to our equation (37). If M1 coupling were considered, $\underset{\sim}{R}^{5}$ of equation (24) and hence the Mueller matrix would not be entirely functions of the scatterer, but would contain a polar vector (a photon wavevector). Space inversion would then induce a non-trivial symmetry for the Mueller matrix, and of course disallow chiral effects from E1--M1 mixing.

A systematic approach to determining symmetries of the Mueller matrix would consist of expanding equation (33) for each symmetry group and scattering geometry, and then using the constraints on $T_{\rho\rho'\sigma\sigma'}$ appropriate to the group. The constraints given in the supplementary publication are limited to symmetric TRI scatterers and of course E1 coupling.

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Captions to figures

Figure 1 Relationships between geometrical factors in different bases. For clarity we omit symmetrisations and the formation of point group invariant reductions.

Figure 2 Connections between experimental and irreducible Raman spectra. The connection $F^{-1}{}_{j_1 j_2 j m, \beta}$ from experimental to spherically based irreducible spectra is given in tables 3, 4 of this paper; all other transformations are given in the supplementary publication.

Table 1 Independent measurements required for general symmetry ($G = C_1$). For the case of TRI scatterers, only the block diagonal part is required, i.e. cross terms involving G——I and X——F are zero. For the case of symmetric scatterers, the matrix is symmetric. For symmetric TRI scatterers, a circle (^{o}) denotes that circular polarisation studies are required, a double bar (") that 180^{o} scattering geometry is required (since $e_\rho e_\rho' \neq 0$ for only one ρ), and a right angle ($^{\perp}$) that 90^{o} scattering geometry is required (since there is no ρ value such that both e_ρ and e_ρ' vanish).

XX	XY	XZ	$XD^{\perp}$	XE	XF	XG	XH	XI
YX	YY	YZ	YD	$YE^{\perp}$	YF	YG	YH	YI
ZX	ZY	ZZ	ZD	ZE	$ZF^{\perp}$	ZG	ZH	ZI
$DX^{\perp}$	DY	DZ	DD"	$DE^{\perp}$	$DF^{\perp}$	DG	DH	DI
EX	$EY^{\perp}$	EZ	$ED^{\perp}$	EE"	$EF^{\perp}$	EG	EH	EI
FX	FY	$FZ^{\perp}$	$FD^{\perp}$	$FE^{\perp}$	FF"	FG	FH	FI
GX	GY	GZ	GD	GE	GF	$GG^{o"}$	$GH^{o\perp}$	$GI^{o\perp}$
HX	HY	HZ	HD	HE	HF	$HG^{o\perp}$	$HH^{o"}$	$HI^{o\perp}$
IX	IY	IZ	ID	IE	IF	$IG^{o\perp}$	$IH^{o\perp}$	$II^{o"}$

Capital letters represent the following choice of polarisation vectors :

X = (1 0 0), Y = (0 1 0), Z = (0 0 1), D = $(1/\sqrt{2})$(0 1 1),

E = $(1/\sqrt{2})$(1 0 1), F = $(1/\sqrt{2})$(1 1 0), G = $(1/\sqrt{2})$(0 1 i),

H = $(1/\sqrt{2})$(1 0 i), I = $(1/\sqrt{2})$(1 i 0).

Table 2 Nonvanishing terms $c^{\eta\varepsilon}_{j_1 j_2 j m\theta}(\Omega)$ in the standard coupling for each group. Only those terms with $\eta = \varepsilon = 1$ are required for symmetric TRI scatterers, and only those with $\varepsilon = 1$ or $\eta = 1$ for symmetric or TRI scatterers respectively. Nonvanishing terms $c'^{\eta\varepsilon}_{j_1 j_2 j m\theta}(\Omega)$ in the alternative coupling are obtained by exchanging η and ε throughout. A label $\theta = c$ represents the linear combination

$$|4c> = [\sqrt{7}|4\ 0> + \sqrt{5}|4\ 4+>]/2\sqrt{3}$$

C_1 symmetry :

(N = 81, N^{+} = 45, N^{++} = 27)

η	ε	j_1	j_2	j	$m\theta$
+	+	0	0	0	0
+	+	1	1	0	0
+	+	2	2	0	0
+	+	1	1	2	(0,1±, 2±)
±	+	2	0	2	(0,1±, 2±)
+	+	2	2	2	(0,1±, 2±)
+	+	2	2	4	(0,1±, 2±, 3±, 4±)
±	-	1	0	1	(0,1±)
±	-	2	1	1	(0,1±)
±	-	2	1	2	(0,1±, 2±)
±	-	2	1	3	(0,1±, 2±, 3±)
-	+	1	1	1	(0,1±)
-	+	2	2	1	(0,1±)
-	+	2	2	3	(0,1±, 2±, 3±)

C_2, C_4, C_{2h}

(N = 41, N^+ = 25, N^{++}= 17)

As for C_1, with the restriction m = 0 mod 2.

C_3, C_{3i}

(N = 27, N^+ = 15, N^{++}= 9)

As for C_1, with the restriction m = 0 mod 3.

C_4, C_{4i}

(N = 21, N^+ = 13, N^{++}= 9)

As for C_1, with the restriction m = 0 mod 4.

C_6, C_{6h}, C_{3h}

(N = 19, N^+ = 11, N^{++}= 7)

As for C_1, with the restriction m = 0.

D_2, D_{2h}, C_{2v}

(N = 21, N^+ = 15, N^{++}= 12)

η	ε	j_1	j_2	j	mθ
+	+	0	0	0	0
+	+	1	1	0	0
+	+	2	2	0	0
+	+	1	1	2	(0,2+)
±	+	2	0	2	(0,2+)
+	+	2	2	2	(0,2+)
+	+	2	2	4	(0,2+,4+)
±	-	2	1	2	(0,2+)
±	-	2	1	3	2 -
-	+	2	2	3	2 -

D_3, C_{3v}, D_{3d}

(N = 14, N^+ = 10, N^{++}= 8)

η	ε	j_1	j_2	j	mθ
+	+	0	0	0	0
+	+	1	1	0	0
+	+	2	2	0	0
+	+	1	1	2	0
±	+	2	0	2	0
+	+	2	2	2	0
+	+	2	2	4	(0,3-)
±	-	2	1	2	0
±	-	2	1	3	3+
-	+	2	2	3	3+

D_4, D_{2d}, D_{4h}, C_{4v}

(N = 11, N^+ = 9, N^{++}= 8)

As for D_2, with the restriction m = 0 mod 4.

D_6, D_{3h}, D_{6h}, C_{6v}

(N = 10, N^+ = 8, N^{++}= 7)

As for D_2, with the restriction m = 0.

T, T_h

($N = 7$, $N^+ = 5$, $N^{++} = 4$)

η	ε	j_1	j_2	j	$m\theta$
+	+	0	0	0	0
+	+	1	1	0	0
+	+	2	2	0	0
+	+	2	2	4	c
±	−	2	1	3	2 −
−	+	2	2	3	2 −

O, O_h, T_d

($N = N^+ = N^{++} = 4$)

η	ε	j_1	j_2	j	$m\theta$
+	+	0	0	0	0
+	+	1	1	0	0
+	+	2	2	0	0
+	+	2	2	4	c

R_3, K

($N = N^+ = N^{++} = 3$)

η	ε	j_1	j_2	j	$m\theta$
+	+	0	0	0	0
+	+	1	1	0	0
+	+	2	2	0	0

Table 3 Linear relationships between intensities of scattering in differing experimental arrangements in all point group symmetries.

C_2, C_s, C_{2h}

$XE = \frac{1}{2}(XX + XZ)$, $YD = \frac{1}{2}(YY + YZ)$, $ZE = \frac{1}{2}(ZZ + XZ)$,
$ZD = \frac{1}{2}(ZZ + YZ)$, $XD = \frac{1}{2}(XY + XZ)$, $YE = \frac{1}{2}(XY + YZ)$,
$DF = \frac{1}{2}(YF + ZF)$, $EF = \frac{1}{2}(XF + ZF)$,
$GI = \frac{1}{4}(YY + XY + XZ + YZ)$, $HI = \frac{1}{4}(XX + XY + XZ + YZ)$.

C_3, C_{3i}

$XF = YF = \frac{1}{2}(XX + XY)$, $DF = \frac{1}{4}(XX + 4YE - XY)$,
$XE = \frac{1}{2}(XX + XY + 2XZ - 2YE)$, $GI = HI = \frac{1}{4}(XX + XY + 2XZ)$,
$YD = \frac{1}{2}(XX - 2XD + XY + XZ)$, $EF = \frac{1}{4}(XX + 4XD - XY)$,
$ZE = ZD = \frac{1}{2}(ZZ + XZ)$, $DE = \frac{1}{4}(ZZ + 2XD + 2YE - XY)$,
$EE = DD - YE + XD$, $GH = \frac{1}{4}(ZZ + XY + 2XZ)$,
$YY = FF = XX$, $YZ = ZF = XZ$, $HH = GG$.

C_4, C_{4h}, S_4

$YD = XE = \frac{1}{2}(XX + XZ)$, $YF = (XX + XY - XF)$,
$ZE = ZD = \frac{1}{2}(ZZ + XZ)$, $GI = HI = \frac{1}{4}(XX + XY + 2XZ)$,
$XD = YE = \frac{1}{2}(XY + XZ)$, $DE = GH = \frac{1}{4}(ZZ + XY + 2XZ)$,
$DF = \frac{1}{2}(YF + XZ)$, $YY = XX$,
$EF = \frac{1}{2}(XF + XZ)$, $YZ = ZF = XZ$,
$GG = HH$, $DD = EE$.

C_6, C_{6h}, C_{3h} ; D_6, D_{3h}, D_{6h}, C_{6v}

$XE = YD = \frac{1}{2}(XX + XZ)$, $XD = YE = \frac{1}{2}(XY + XZ)$,

$XF = YF = \frac{1}{2}(XX + XY)$, $DF = GI = EF = HI = \frac{1}{4}(XX + XY + 2XZ)$,

$ZE = ZD = \frac{1}{2}(ZZ + XZ)$, $GH = DE = \frac{1}{4}(ZZ + XY + 2XZ)$,

$YY = FF = XX$, $YZ = ZF = XZ$, $DD = EE$, $HH = GG$.

D_2, D_{2h}, C_{2v}

$XE = \frac{1}{2}(XX + XZ)$, $XD = \frac{1}{2}(XY + XZ)$,

$XF = \frac{1}{2}(XX + XY)$, $YE = \frac{1}{2}(XY + YZ)$,

$YD = \frac{1}{2}(YY + YZ)$, $ZF = \frac{1}{2}(XZ + YZ)$,

$YF = \frac{1}{2}(YY + XY)$, $DF = GI = \frac{1}{4}(XX + XY + XZ + YZ)$,

$ZE = \frac{1}{2}(ZZ + XZ)$, $EF = HI = \frac{1}{4}(YY + XY + XZ + YZ)$,

$ZD = \frac{1}{2}(ZZ + YZ)$, $DE = GH = \frac{1}{4}(ZZ + XY + XZ + YZ)$.

D_3, C_{3v}, D_{3d}

$YY = FF = XX$, $YZ = ZF = XZ$, $HH = GG$,

$XE = \frac{1}{2}(XX - 2YE + 2XZ + XY)$, $XD = \frac{1}{2}(XY + XZ)$,

$XF = YF = \frac{1}{2}(XX + XY)$, $DF = \frac{1}{4}(XX + 4YE - XY)$,

$YD = \frac{1}{2}(XX + XZ)$, $GI = EF = HI = \frac{1}{4}(XX + XY + 2XZ)$,

$ZD = ZE = \frac{1}{2}(ZZ + XZ)$, $GH = \frac{1}{4}(ZZ + XY + 2XZ)$,

$EE = \frac{1}{2}(2DD - 2YE + XZ + XY)$, $DE = \frac{1}{4}(ZZ + 2YE + XZ)$.

D_4, D_{2d}, D_{4h}, C_{4v}

$XE = YD = \frac{1}{2}(XX + XZ)$, $XD = YE = \frac{1}{2}(XY + XZ)$,

$XF = YF = \frac{1}{2}(XX + XY)$, $DF = GI = EF = HI = \frac{1}{4}(XX + XY + 2XZ)$,

$ZE = ZD = \frac{1}{2}(ZZ + XZ)$, $DE = GH = \frac{1}{4}(ZZ + XY + 2XZ)$,

$YY = XX$, $YZ = ZF = XZ$, $DD = EE$, $GG = HH$.

O, O_h, T, T_d T_h

$XE = XF = YD = YF = ZE = ZD = \frac{1}{2}(XX + XY)$,

$DF = HI = EF = GI = DE = GH = \frac{1}{4}(XX + 3XY)$,

$YY = ZZ = XX$, $XZ = YZ = XD = YE = ZF = XY$,

$EE = FF = DD$, $HH = II = GG$.

K, R_3

$XE = XF = YD = YF = ZE = ZD = \frac{1}{2}(XX + XY)$,

$DF = HI = EF = GI = DE = GH = \frac{1}{4}(XX + 3XY)$,

$YY = ZZ = DD = EE = FF = XX$,

$XZ = YZ = XD = YE = ZF = XY$,

$II = HH = GG$.

Table 4. Transformation from the experimental spectra in the spherical basis for real symmetric scatterers in the case of no assumed symmetry ($G = C_1$). This may be simplified greatly for any choice of point group symmetry by inserting the corresponding restrictions (table 3) on the experimental spectra.

	XX	XY	XZ	XD	XE	XF	YY	YZ	YD	YE	YF	ZZ	ZD	ZE	ZF	DD	DE	DF	EE	EF	FF	GG	GH	GI	HH	HI	II
00 00	1	$\frac{2}{3}$	$\frac{2}{3}$	-	$\frac{-2}{3}$	$\frac{-2}{3}$	1	$\frac{2}{3}$	$\frac{-2}{3}$	-	$\frac{-2}{3}$	1	$\frac{-2}{3}$	$\frac{-2}{3}$	-	$\frac{2}{3}$	-	-	$\frac{2}{3}$	-	$\frac{2}{3}$	$\frac{-2}{3}$	-	-	$\frac{-2}{3}$	-	$\frac{-2}{3}$
02 20	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{-1}{3}$	-	$\frac{1}{3}$	$\frac{-2}{3}$	$\frac{1}{2}$	$\frac{-1}{3}$	$\frac{1}{3}$	-	$\frac{-2}{3}$	-1	$\frac{1}{3}$	$\frac{1}{3}$	-	$\frac{-1}{3}$	-	-	$\frac{-1}{3}$	-	$\frac{2}{3}$	$\frac{1}{3}$	-	-	$\frac{1}{3}$	-	$\frac{-2}{3}$
02 21+	$\frac{1}{\sqrt{3}}$	-	$\frac{2}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{-2}{\sqrt{3}}$	-	-	-	$\frac{1}{\sqrt{3}}$	-	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	$\frac{-2}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	-	$\frac{-2}{\sqrt{3}}$	-	-	-	-	-	$\frac{-2}{\sqrt{3}}$	-	-	-
02 21-	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	$\frac{-1}{\sqrt{3}}$	$\frac{-1}{\sqrt{3}}$	$\frac{-1}{\sqrt{3}}$	$\frac{-1}{\sqrt{3}}$	$\frac{2}{\sqrt{3}}$	$\frac{-1}{\sqrt{3}}$	-	$\frac{-1}{\sqrt{3}}$	$\frac{2}{\sqrt{3}}$	-	$\frac{-1}{\sqrt{3}}$	-	-	-	-	$\frac{2}{\sqrt{3}}$	-	-	-	-	$\frac{-2}{\sqrt{3}}$	-
02 22+	$\frac{-3}{2\sqrt{3}}$	-	$\frac{-1}{\sqrt{3}}$	-	$\frac{1}{\sqrt{3}}$	-	$\frac{3}{2\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{-1}{\sqrt{3}}$	-	-	-	$\frac{-1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	$\frac{1}{\sqrt{3}}$	-	-	$\frac{-1}{\sqrt{3}}$	-	-	$\frac{-1}{\sqrt{3}}$	-	-	$\frac{1}{\sqrt{3}}$	-	-
02 22-	$\frac{-1}{\sqrt{3}}$	$\frac{-1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{-1}{\sqrt{3}}$	-	$\frac{2}{\sqrt{3}}$	$\frac{-1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	$\frac{-1}{\sqrt{3}}$	$\frac{2}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{-1}{\sqrt{3}}$	$\frac{-1}{\sqrt{3}}$	-	-	$\frac{2}{\sqrt{3}}$	-	-	-	-	-	$\frac{-2}{\sqrt{3}}$	-	-	-
11 00	-	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	$\frac{1}{\sqrt{3}}$	-	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	$\frac{-1}{\sqrt{3}}$	-	-	$\frac{-1}{\sqrt{3}}$	-	$\frac{-1}{\sqrt{3}}$	$\frac{-1}{\sqrt{3}}$	-	-	$\frac{-1}{\sqrt{3}}$	-	$\frac{-1}{\sqrt{3}}$
11 20	-	$\frac{-2}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	-	$\frac{1}{\sqrt{6}}$	$\frac{-2}{\sqrt{6}}$	-	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	-	$\frac{-2}{\sqrt{6}}$	-	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	-	$\frac{-1}{\sqrt{6}}$	-	-	$\frac{-1}{\sqrt{6}}$	-	$\frac{2}{\sqrt{6}}$	$\frac{-1}{\sqrt{6}}$	-	-	$\frac{-1}{\sqrt{6}}$	-	$\frac{2}{\sqrt{6}}$
11 21+	-	$\frac{-2}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-	-	$\frac{-1}{\sqrt{2}}$	$\frac{-2}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-	-	-	$\frac{1}{\sqrt{2}}$	-	-	$\frac{-2}{\sqrt{2}}$	-	-	-	-	$\frac{2}{\sqrt{2}}$	-	-	-
11 21-	-	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	$\frac{-2}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	-	$\frac{-1}{\sqrt{2}}$	-	-	-	-	$\frac{-1}{\sqrt{2}}$	-	-	-	-	$\frac{2}{\sqrt{2}}$	-	-	-	-	-	$\frac{2}{\sqrt{2}}$	-
11 22+	-	-	$\frac{1}{\sqrt{2}}$	-	$\frac{1}{\sqrt{2}}$	-	-	$\frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	-	$\frac{-1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-	$\frac{1}{\sqrt{2}}$	-	-	$\frac{-1}{\sqrt{2}}$	-	-	$\frac{1}{\sqrt{2}}$	-	-	$\frac{-1}{\sqrt{2}}$	-	-
11 22-	-	-	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	-	$\frac{1}{\sqrt{2}}$	-	$\frac{-1}{\sqrt{2}}$	-	-	$\frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	$\frac{-2}{\sqrt{2}}$	-	$\frac{2}{\sqrt{2}}$	-	-	-	-	-	$\frac{2}{\sqrt{2}}$	-	-	-	-
22 00	-	$\frac{1}{3\sqrt{5}}$	$\frac{1}{3\sqrt{5}}$	-	$\frac{-1}{3\sqrt{5}}$	$\frac{-1}{3\sqrt{5}}$	-	$\frac{1}{3\sqrt{5}}$	$\frac{-1}{3\sqrt{5}}$	-	$\frac{-1}{3\sqrt{5}}$	-	$\frac{-1}{3\sqrt{5}}$	$\frac{-1}{3\sqrt{5}}$	-	$\frac{1}{3\sqrt{5}}$	-	-	$\frac{1}{3\sqrt{5}}$	-	$\frac{1}{3\sqrt{5}}$	$\frac{5}{3\sqrt{5}}$	-	-	$\frac{5}{3\sqrt{5}}$	-	$\frac{5}{3\sqrt{5}}$
22 20	-	$\frac{-2}{3\sqrt{14}}$	$\frac{1}{3\sqrt{14}}$	-	$\frac{-1}{3\sqrt{14}}$	$\frac{2}{3\sqrt{14}}$	-	$\frac{1}{3\sqrt{14}}$	$\frac{-1}{3\sqrt{14}}$	-	$\frac{2}{3\sqrt{14}}$	-	$\frac{-1}{3\sqrt{14}}$	$\frac{-1}{3\sqrt{14}}$	-	$\frac{1}{3\sqrt{14}}$	-	-	$\frac{1}{3\sqrt{14}}$	-	$\frac{-2}{3\sqrt{14}}$	$\frac{-7}{3\sqrt{14}}$	-	-	$\frac{-7}{3\sqrt{14}}$	-	$\frac{14}{3\sqrt{14}}$
22 21+	$\frac{2}{\sqrt{42}}$	-	$\frac{1}{\sqrt{42}}$	$\frac{-1}{\sqrt{42}}$	$\frac{-4}{\sqrt{42}}$	-	$\frac{3}{\sqrt{42}}$	-	$\frac{-1}{\sqrt{42}}$	$\frac{-6}{\sqrt{42}}$	$\frac{-1}{\sqrt{42}}$	$\frac{2}{\sqrt{42}}$	-	$\frac{-4}{\sqrt{42}}$	$\frac{-1}{\sqrt{42}}$	-	-	$\frac{2}{\sqrt{42}}$	-	-	-	-	$\frac{14}{\sqrt{42}}$	-	-	-	-
22 21-	$\frac{-4}{\sqrt{42}}$	$\frac{-7}{\sqrt{42}}$	$\frac{-7}{\sqrt{42}}$	$\frac{6}{\sqrt{42}}$	$\frac{1}{\sqrt{42}}$	$\frac{1}{\sqrt{42}}$	$\frac{-2}{\sqrt{42}}$	$\frac{-8}{\sqrt{42}}$	$\frac{4}{\sqrt{42}}$	$\frac{1}{\sqrt{42}}$	-	$\frac{-2}{\sqrt{42}}$	$\frac{4}{\sqrt{42}}$	-	$\frac{1}{\sqrt{42}}$	-	-	-	-	$\frac{-2}{\sqrt{42}}$	-	-	-	-	-	$\frac{14}{\sqrt{42}}$	-
22 22+	-	-	$\frac{1}{\sqrt{42}}$	-	$\frac{-1}{\sqrt{42}}$	-	-	$\frac{-1}{\sqrt{42}}$	$\frac{1}{\sqrt{42}}$	-	-	-	$\frac{1}{\sqrt{42}}$	$\frac{-1}{\sqrt{42}}$	-	$\frac{-1}{\sqrt{42}}$	-	-	$\frac{1}{\sqrt{42}}$	-	-	$\frac{7}{\sqrt{42}}$	-	-	$\frac{-7}{\sqrt{42}}$	-	-
22 22-	$\frac{-2}{\sqrt{42}}$	$\frac{-8}{\sqrt{42}}$	$\frac{-7}{\sqrt{42}}$	$\frac{1}{\sqrt{42}}$	-	$\frac{4}{\sqrt{42}}$	$\frac{-2}{\sqrt{42}}$	$\frac{-7}{\sqrt{42}}$	-	$\frac{1}{\sqrt{42}}$	$\frac{4}{\sqrt{42}}$	$\frac{-4}{\sqrt{42}}$	$\frac{1}{\sqrt{42}}$	$\frac{1}{\sqrt{42}}$	$\frac{6}{\sqrt{42}}$	-	$\frac{-2}{\sqrt{42}}$	-	-	-	-	-	$\frac{14}{\sqrt{42}}$	-	-	-	-
22 40	-	$\frac{2}{\sqrt{70}}$	$\frac{-8}{\sqrt{70}}$	-	$\frac{8}{\sqrt{70}}$	$\frac{-2}{\sqrt{70}}$	-	$\frac{-8}{\sqrt{70}}$	$\frac{8}{\sqrt{70}}$	-	$\frac{-2}{\sqrt{70}}$	-	$\frac{8}{\sqrt{70}}$	$\frac{8}{\sqrt{70}}$	-	$\frac{-8}{\sqrt{70}}$	-	-	$\frac{-8}{\sqrt{70}}$	-	$\frac{2}{\sqrt{70}}$	-	-	-	-	-	-
22 41+	$\frac{3}{\sqrt{28}}$	-	$\frac{-2}{\sqrt{28}}$	$\frac{2}{\sqrt{28}}$	$\frac{-6}{\sqrt{28}}$	-	$\frac{-1}{\sqrt{28}}$	-	$\frac{2}{\sqrt{28}}$	$\frac{-2}{\sqrt{28}}$	$\frac{2}{\sqrt{28}}$	$\frac{-4}{\sqrt{28}}$	-	$\frac{8}{\sqrt{28}}$	$\frac{2}{\sqrt{28}}$	-	-	$\frac{4}{\sqrt{28}}$	-	-	-	-	-	-	-	-	-
22 41-	$\frac{1}{\sqrt{28}}$	-	-	$\frac{-2}{\sqrt{28}}$	$\frac{-2}{\sqrt{28}}$	$\frac{-2}{\sqrt{28}}$	$\frac{-3}{\sqrt{28}}$	$\frac{2}{\sqrt{28}}$	$\frac{6}{\sqrt{28}}$	$\frac{-2}{\sqrt{28}}$	-	$\frac{4}{\sqrt{28}}$	$\frac{-8}{\sqrt{28}}$	-	$\frac{-2}{\sqrt{28}}$	-	-	-	-	$\frac{4}{\sqrt{28}}$	-	-	-	-	-	-	-
22 42+	-	-	$\frac{4}{\sqrt{14}}$	-	$\frac{-4}{\sqrt{14}}$	-	-	$\frac{-4}{\sqrt{14}}$	$\frac{4}{\sqrt{14}}$	-	-	-	$\frac{4}{\sqrt{14}}$	$\frac{-4}{\sqrt{14}}$	-	$\frac{-4}{\sqrt{14}}$	-	-	$\frac{4}{\sqrt{14}}$	-	-	-	-	-	-	-	-
22 42-	$\frac{-1}{\sqrt{14}}$	$\frac{-4}{\sqrt{14}}$	-	$\frac{4}{\sqrt{14}}$	-	$\frac{2}{\sqrt{14}}$	$\frac{-1}{\sqrt{14}}$	-	-	$\frac{4}{\sqrt{14}}$	$\frac{2}{\sqrt{14}}$	$\frac{-2}{\sqrt{14}}$	$\frac{4}{\sqrt{14}}$	$\frac{4}{\sqrt{14}}$	$\frac{-4}{\sqrt{14}}$	-	$\frac{-8}{\sqrt{14}}$	-	-	-	-	-	-	-	-	-	-
22 43+	$\frac{-1}{2}$	-	-1	1	1	-	$\frac{-1}{2}$	-	1	-1	1	-	-	-	1	-	-	-2	-	-	-	-	-	-	-	-	-
22 43-	$\frac{-1}{2}$	-	-	-1	1	1	$\frac{-1}{2}$	-1	1	1	-	-	-	-	1	-	-	-	-	-2	-	-	-	-	-	-	-
22 44+	-	$\frac{-2}{\sqrt{2}}$	-	-	-	$\frac{2}{\sqrt{2}}$	-	-	-	-	$\frac{2}{\sqrt{2}}$	-	-	-	-	-	-	-	-	-	$\frac{-2}{\sqrt{2}}$	-	-	-	-	-	-
22 44-	$\frac{1}{\sqrt{2}}$	-	-	-	-	$\frac{-2}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	-	$\frac{2}{\sqrt{2}}$	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
c	-	$\frac{-4}{\sqrt{30}}$	$\frac{-4}{\sqrt{30}}$	-	$\frac{4}{\sqrt{30}}$	$\frac{4}{\sqrt{30}}$	-	$\frac{-4}{\sqrt{30}}$	$\frac{4}{\sqrt{30}}$	-	$\frac{4}{\sqrt{30}}$	-	$\frac{4}{\sqrt{30}}$	$\frac{4}{\sqrt{30}}$	-	$\frac{-4}{\sqrt{30}}$	-	-	$\frac{-4}{\sqrt{30}}$	-	$\frac{-4}{\sqrt{30}}$	-	-	-	-	-	-

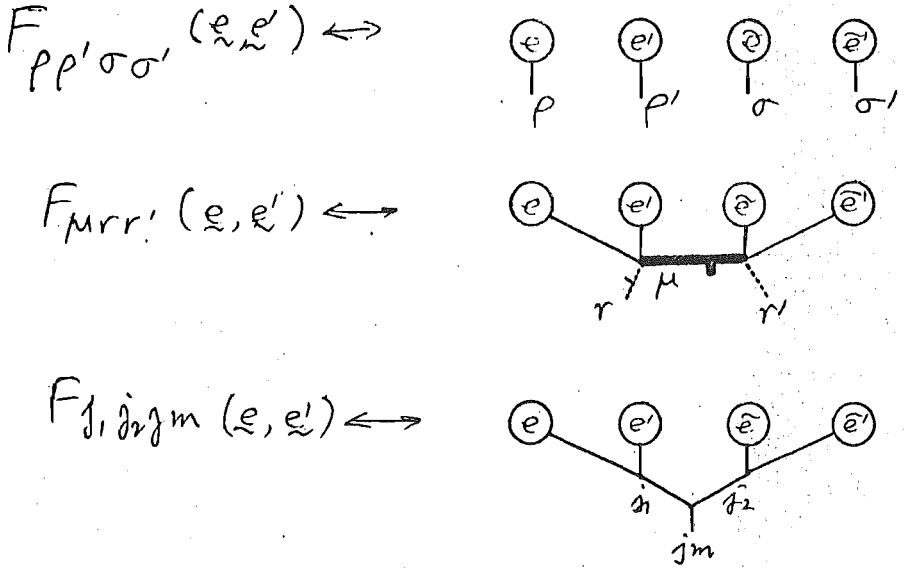

Fig 1 Chandra

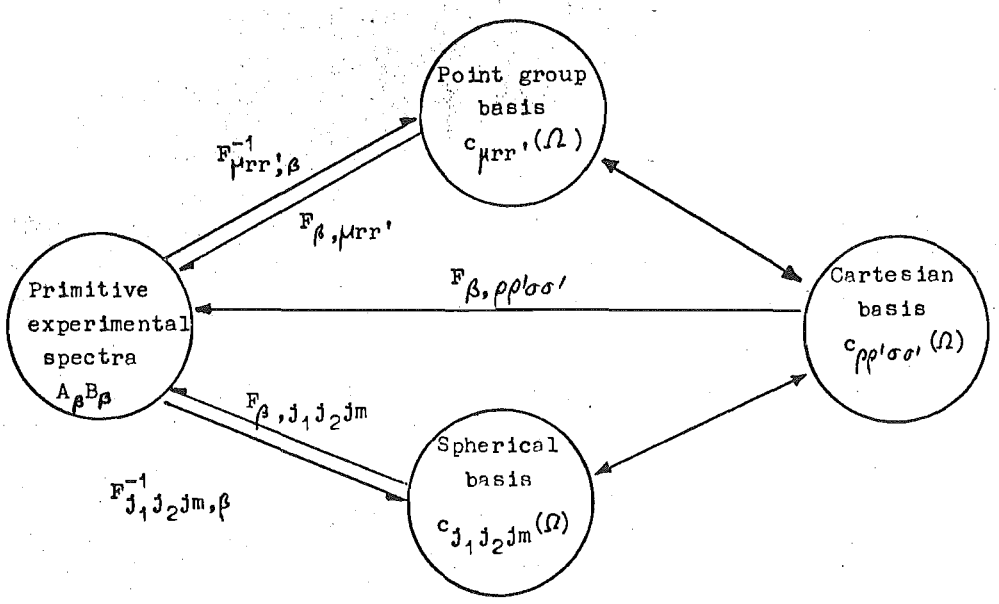

Figure 2 : Chandra et al

Supplementary publication to :

Irreducible analysis of Raman spectra for all crystal point groups

Clare D Churcher and G E Stedman

(J Phys C: Solid State Phys (1981))

1 Introduction

The text and tables listed here complement and extend the above reference, for users requiring transformation tables between different bases for the description of Raman spectra or the transformation from experimental to irreducible spectra in any basis.

In §2 we define the basis choices for irreducible spectra in the spherical and the point group basis. In §3 we list the transformations between experimental and irreducible spectra in several bases and all point group symmetries.

2 Symmetrisation of spectra in spherical and point group bases

2.1 Spherical basis

We define the symmetrised geometrical factor $F^{\eta\epsilon}_{j_1 j_2 jm\theta}(\underset{\sim}{e}, \underset{\sim}{e}')$ along the lines of equation (4) of the main paper. First, $[\underset{\sim}{e}\ \underset{\sim}{e}']_{j_1 j_2 jm}$ is defined from $[\underset{\sim}{e}\ \underset{\sim}{e}']_{\rho\rho'\sigma\sigma'}$ by a unitary transformation:

$$[\underset{\sim}{e}\ \underset{\sim}{e}']_{\rho\rho'\sigma\sigma'} = \Sigma_{j_1 j_2 jm}\ T^{j_1 j_2 jm}_{\rho\rho'\sigma\sigma'}\ [\underset{\sim}{e}\ \underset{\sim}{e}']_{j_1 j_2 jm} \qquad (1)$$

$$T^{j_1 j_2 jm}_{\rho\rho'\sigma\sigma'} = \Sigma_{\bar{m}m' nn' m_1 m_2} \langle 1\bar{m}|1\rho\rangle\langle 1m'|1\rho'\rangle\langle 1n|1\sigma\rangle\langle 1n'|1\sigma'\rangle \hat{j}_1\hat{j}_2\hat{j}$$
$$(-1)^{j_1+j_2+j}\begin{pmatrix}1 & 1 & j_1\\ \bar{m} & m' & -m_1\end{pmatrix}\begin{pmatrix}1 & 1 & j\\ n & n' & -m_2\end{pmatrix}\begin{pmatrix}j_1 & j_2 & j\\ m_1 & m_2 & -m\end{pmatrix} \qquad (2)$$

where $\hat{j} = (2j+1)^{\frac{1}{2}}$. The symmetries

$$T^{j_1 j_2 jm}_{\rho\rho'\sigma\sigma'} = \{1\ 1\ j_1\}\{1\ 1\ j_2\}\ T^{j_1 j_2 jm}_{\rho'\rho\sigma'\sigma} \qquad (3)$$

$$= \{j_1\ j_2\ j\}\ T^{j_2 j_1 jm}_{\sigma\sigma'\rho\rho'} \qquad (4)$$

$$= (-1)^{j-m}\left(T^{j_1 j_2 j-m}_{\rho\rho'\sigma\sigma'}\right)^* \qquad (5)$$

motivate the symmetrised definition

$$T^{\eta\epsilon j_1 j_2 jm}_{\rho\rho'\sigma\sigma'} = (2kg)^{-1}\ (1+\epsilon(-1)^{j_1+j_2})\left[T^{j_1 j_2 jm}_{\rho\rho'\sigma\sigma'} + \eta\,(-1)^{j_1+j_2+j}\ T^{j_2 j_1 jm}_{\rho\rho'\sigma\sigma'}\right] \qquad (6)$$

where $g=\sqrt{2}$ if $j_1 \neq j_2$, and g=2 otherwise. We also define

$$F^{\eta\epsilon}_{j_1 j_2 jm}(\underset{\sim}{e}, \underset{\sim}{e}') = T^{\rho\rho'\sigma\sigma'}_{\eta\epsilon j_1 j_2 jm}[\underset{\sim}{e}\ \underset{\sim}{e}']^{\eta\epsilon}_{\rho\rho'\sigma\sigma'} \qquad (7)$$

The symmetrised transformation (equation 6 above) relates the symmetrised geometrical factors of equation (7) above and equation (8) of the main script. Finally we make the unitary transformation to real combinations of +m and -m (using (5) and writing f^{jm} for $T^{\eta\epsilon j_1 j_2 jm}_{\rho\rho'\sigma\sigma'}$ etc)

$$\begin{aligned} f^{jm\theta} &= (1/\sqrt{2})\left[(-1)^{j-m}f^{jm} + f^{j-m}\right], && m>0,\ \theta = +\\ &= (1/\sqrt{2}i)\left[(-1)^{j-m}f^{jm} - f^{j-m}\right] && m>0,\ \theta = -\\ &= f^{jm}, && m=0. \end{aligned} \qquad (8)$$

We then identify the fully symmetrised geometrical factor

$$F^{\eta\epsilon}_{\alpha}(\underset{\sim}{e}, \underset{\sim}{e}') = [\underset{\sim}{e}\ \underset{\sim}{e}']^{\eta\epsilon}_{j_1 j_2 jm\theta} \qquad (9)$$

2.2 Point group basis

The unitary transformation coefficients between the cartesian and point group bases have the symmetries (cf. I)

$$T^{\mu rr'}_{\rho\rho'\sigma\sigma'} = \{1\ 1\ \mu\ r\}\{1\ 1\ \mu\ r'\}\ T^{\mu rr'}_{\rho'\rho\sigma'\sigma} \qquad (10)$$

$$= \varepsilon^{\mu}_{r}\ \varepsilon^{\mu}_{r'}\ T^{\mu^* r' r}_{\sigma\sigma'\rho\rho'} \qquad (11)$$

$$= \varepsilon^{\mu}_{r}\ \varepsilon^{\mu}_{r'}\ (T^{\mu^* rr'}_{\rho\rho'\sigma\sigma'})^* \qquad (12)$$

Symmetrising as in equation (4) of the main paper, we define the transformation to real constants:

$$T^{\eta\epsilon\mu rr'\xi}_{\rho\rho'\sigma\sigma'} = (2kk')^{-1}\left[1 + \epsilon\{1\ 1\ \mu\ r\}\{1\ 1\ \mu\ r'\}\right]\theta \times \left[(T^{\mu rr'}_{\rho\rho'\sigma\sigma'} + T^{\mu^* r'r}_{\rho\rho'\sigma\sigma'}) + \xi(T^{\mu^* rr'}_{\rho\rho'\sigma\sigma'} + \alpha T^{\mu r'r}_{\rho\rho'\sigma\sigma'})\right] \qquad (13)$$

where $\alpha = \eta\varepsilon^{\mu}_{r}\varepsilon^{\mu}_{r'}$, and $k' = 4$ if $\mu = \mu^*$ and $r = r'$, $k' = 2\sqrt{2}$ if $\mu = \mu^*$ or $r = r'$, and $k' = 2$ if $\mu \neq \mu^*$ and $r \neq r'$. $\theta = 1(i)$ as $\sum_{r}\xi^{\mu}_{r}\xi^{\mu}_{r'} = +1\ (-1)$. The associated geometrical factors are real and are given by

$$F^{\eta\epsilon}_{\mu rr'\xi}(\underset{\sim}{e}, \underset{\sim}{e}') = \sum_{\rho\rho'\sigma\sigma'}\left[\underset{\sim}{e}\ \underset{\sim}{e}'\right]^{\eta\epsilon}_{\rho\rho'\sigma\sigma'} T^{\rho\rho'\sigma\sigma'}_{\eta\epsilon\mu rr'\xi} \qquad (14)$$

where we write $T^{\alpha}_{\alpha'}$ for $(T^{\alpha'}_{\alpha})^{-1}$. The intensity (equation 4 of the main paper) has a sum over $\alpha = (\mu rr'\xi)$, where the summation is restricted to $r' \geq r$, and only one of μ, μ^* if $\mu \neq \mu^*$. Also, if $\mu = \mu^*$, $\xi = 1$ only; if $r = r'$, $\eta = 1$ only. Obviously the symmetrisation restriction $\{1\ 1\ \mu\ r\}\{1\ 1\ \mu\ r'\} = \varepsilon$ agrees with I.

We note that the symmetrised quantities defined in I are related to those defined here by

$$\tilde{T}^{\mu rr'}_{\rho\rho'\sigma\sigma'} = q\ T^{++\mu rr'+}_{\rho\rho'\sigma\sigma'} \qquad (15)$$

with $q = 1$ if $\mu = \mu^*$ and $r = r'$, and $q = \sqrt{2}$ if $\mu = \mu^*$ or $r = r'$. In the exceptional case where $\mu \neq \mu^*$ and $r \neq r'$ (C_3, $\mu = 1$)

$$\tilde{T}^{101}_{\rho\rho'\sigma\sigma'} = 2\ T^{++101+}_{\rho\rho'\sigma\sigma'} \qquad (16)$$

$$\tilde{T}^{110}_{\rho\rho'\sigma\sigma'} = 2\ T^{++101-}_{\rho\rho'\sigma\sigma'} \qquad (17)$$

All these restrictions have the effect of limiting the number of terms in the irreducible expansion of the intensity (equation 1 of the main script) to the same value, appropriate to each physical choice, as in any other basis. Counting up the terms implied by the above restrictions we find

$$N^{\eta\epsilon} = \tfrac{1}{2}\sum_{\mu}\left[(1 - \epsilon)n^{+}_{\mu}n^{-}_{\mu} + \tfrac{1}{2}(1 + \epsilon)(n^{+2}_{\mu} + n^{-2}_{\mu} + \eta\, n_{\mu}\delta_{\mu\mu^*})\right] \qquad (18)$$

where $N^{\eta\epsilon}$ refers to the number of terms in the irreducible expansion with symmetry choices η, ϵ respectively. (Thus N of the main script $= \sum_{\eta\epsilon} N^{\eta\epsilon}$, $N^{+} = \sum_{\epsilon} N^{+\epsilon}$.) We also have defined n^{λ}_{μ} as the number of times irrep μ appears in $[1 \times 1]_{\lambda}$, and $n_{\mu} = \sum_{\lambda} n^{\lambda}_{\mu}$. Equation (3) of the main script implies the existence of a curious combinatoric restriction on these multiplicities in all point groups, viz:

$$\sum_{\mu}\left[(n^{+}_{\mu} - n^{-}_{\mu})^2 - n_{\mu}\delta_{\mu\mu^*}\right] = 0 \qquad (19)$$

which has no obvious explanation in the point group basis. In detail,

$$N^{++} = \tfrac{1}{2}\sum_{\mu}\left[n^{+2}_{\mu} + n^{-2}_{\mu} + n_{\mu}\delta_{\mu\mu^*}\right]$$

$$N^{+-} = N^{-+} = N^{--} = \sum_{\mu} n^{+}_{\mu}n^{-}_{\mu}$$

so that $N^{--} = 0$ in $G = 0$ since no irrep appears in both $[1 \times 1]_{+}$ and $[1 \times 1]_{-}$, for example.

3 Tables and transformations

Table 1 gives the transformation $T^{++j_1j_2jm\Theta}_{\rho\rho'\sigma\sigma'}$

It was noted in I that for symmetric TRI scatterers the cartesian components zzyz and zzzx are always zero for non-trivial symmetry. From table 1 we note that this corresponds to the absence of spherical parameters with m = 1. This in turn indicates also that $F_{xxyz} = F_{xyzx} = F_{xyxz} = -F_{yyyz}$, and that $F_{yyzx} = F_{xyyz} = F_{xyzy} = -F_{xxzx}$ for all groups.

Tables 2 and 3 give the matrices $F_{\beta,++\mu rr'\xi}$ and their inverses respectively.. (Each arrangement $A_\beta B_\beta$ was substituted into the tables of I to give $F_{\beta,++\mu rr'}$ and the inverse was obtained by using exact arithmetic computer routines.)

Table 4 gives the transformation $T^{++\mu rr'\xi}_{\rho\rho'\sigma\sigma'}$, and also lists the relationships between the choices of cartesian labels (themselves also symmetrised) associated with each point group symmetry. The direct transformation to experiment from cartesian spectra is given in table 5 in the case of no assumed symmetry ($G = C_1$); in any particular symmetry, the relations of table 4 between cartesian components should be used to simplify table 5.

Multiplication of the corresponding matrices in tables 3 and 4 would give $F^{-1}_{\rho\rho',\sigma\sigma',\beta}$ directly.

Table 6 gives $F_{\beta,++j_1j_2jm\Theta}$ for the case $G = C_1$. Again this may be simplified using table 2 of the main paper. The inverse, $F^{-1}_{++j_1j_2jm\Theta,\beta}$ is given in the main paper.

The generalisation of these tables to the case of asymmetric scattering is straightforward in principle. It is necessary to consider an enlarged set of primitive experimental arrangements ($N_s^+ \rightarrow N^+$), with $A_\beta B_\beta \neq B_\beta A_\beta$. Adding $B_\beta A_\beta$ to each nondiagonal $A_\beta B_\beta$ in table 5 would not be adequate, our choice of primitive arrangements being arbitrary in this connection. In C_6 for example, one would have to introduce two new nondiagonal primitive arrangements (perhaps replacing ZZ by GH, XX by DF) whose asymmetry was now observable.

Table 1 Transformation from spherical to cartesian basis for symmetric TRI scatterers in any symmetry.

The inverse transformation is given by the transpose.

The label mθ = 4c denotes the cubic invariant:

$$|4c\rangle = \{\sqrt{7}|4\ 0\rangle + \sqrt{5}|4\ 4\ +\rangle\}/2\sqrt{3}$$

(Table 1)

	j_1	0	0	0	0	0	0	1	1	1	1	1	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
	j_2	0	2	2	2	2	2	1	1	1	1	1	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
	j	0	2	2	2	2	2	0	2	2	2	2	2	0	2	2	2	2	2	4	4	4	4	4	4	4	4	4	4	4
	$m\theta$	0	0	1+	1-	2+	2-	0	0	1+	1-	2+	2-	0	0	1+	1-	2+	2-	0	1+	1-	2+	2-	3+	3-	4+	4-	c
X X Z X																$-\frac{2}{\sqrt{42}}$														
X Y Y Y														$\frac{2}{3\sqrt{5}}$	$\frac{2}{3\sqrt{14}}$			$-\frac{2}{\sqrt{42}}$		$\frac{3}{2\sqrt{70}}$			$-\frac{1}{\sqrt{14}}$				$\frac{1}{2\sqrt{2}}$		$\frac{2}{\sqrt{30}}$
X Y Y Z		$\frac{\sqrt{2}}{3}$	$\frac{\sqrt{2}}{6}$											$-\frac{2}{3\sqrt{10}}$	$-\frac{4}{3\sqrt{7}}$					$\frac{1}{2\sqrt{35}}$							$-\frac{1}{2}$		$-\frac{1}{\sqrt{5}}$
X Z Z Z		$\frac{\sqrt{2}}{3}$	$-\frac{\sqrt{2}}{6}$			$-\frac{1}{\sqrt{6}}$								$-\frac{2}{3\sqrt{10}}$	$\frac{2}{3\sqrt{7}}$			$\frac{2}{\sqrt{21}}$		$-\frac{2}{\sqrt{35}}$			$\frac{1}{\sqrt{7}}$						$\frac{1}{\sqrt{15}}$
X X X Y							$\frac{1}{\sqrt{3}}$												$\frac{2}{\sqrt{42}}$					$\frac{1}{\sqrt{14}}$				$-\frac{1}{\sqrt{2}}$	
X X Y Z					$\frac{1}{\sqrt{3}}$												$-\frac{4}{\sqrt{42}}$							$\frac{1}{\sqrt{28}}$			$-\frac{1}{2}$			
X X Z X				$-\frac{1}{\sqrt{3}}$												$-\frac{2}{\sqrt{42}}$						$-\frac{3}{\sqrt{28}}$			$\frac{1}{2}$					
Y Y Y Y		$\frac{1}{3}$	$\frac{1}{3}$			$\frac{1}{\sqrt{3}}$								$\frac{2}{3\sqrt{5}}$	$\frac{2}{3\sqrt{14}}$			$\frac{2}{\sqrt{42}}$		$\frac{3}{2\sqrt{70}}$			$\frac{1}{\sqrt{14}}$				$\frac{1}{2\sqrt{2}}$		$\frac{2}{\sqrt{30}}$
Y Y Z Z		$\frac{\sqrt{2}}{3}$	$-\frac{\sqrt{2}}{6}$			$\frac{1}{\sqrt{6}}$								$-\frac{2}{3\sqrt{10}}$	$\frac{2}{3\sqrt{7}}$			$-\frac{2}{\sqrt{21}}$		$-\frac{2}{\sqrt{35}}$			$-\frac{1}{\sqrt{7}}$						$-\frac{1}{\sqrt{15}}$
Y Y X Y							$\frac{1}{\sqrt{3}}$												$\frac{2}{\sqrt{42}}$					$\frac{1}{\sqrt{14}}$				$\frac{1}{\sqrt{2}}$	
Y Y Y Z					$\frac{1}{\sqrt{3}}$												$\frac{2}{\sqrt{42}}$							$\frac{3}{\sqrt{28}}$			$\frac{1}{2}$			
Y Y Z X				$-\frac{1}{\sqrt{3}}$												$\frac{4}{\sqrt{42}}$						$-\frac{1}{\sqrt{28}}$			$-\frac{1}{2}$					
Z Z Z Z		$\frac{1}{3}$	$-\frac{2}{3}$											$\frac{2}{3\sqrt{5}}$	$-\frac{4}{3\sqrt{14}}$					$\frac{4}{\sqrt{70}}$									$\frac{2}{\sqrt{30}}$
Z Z X Y							$\frac{1}{\sqrt{3}}$												$\frac{4}{\sqrt{42}}$					$-\frac{2}{\sqrt{14}}$					
Z Z Y Z					$\frac{1}{\sqrt{3}}$												$\frac{2}{\sqrt{42}}$						$-\frac{2}{\sqrt{7}}$						
Z Z Z X				$-\frac{1}{\sqrt{3}}$												$-\frac{2}{\sqrt{42}}$						$\frac{2}{\sqrt{7}}$								
X Y X Y							$\frac{1}{\sqrt{6}}$		$-\frac{1}{\sqrt{5}}$					$\frac{1}{\sqrt{10}}$	$\frac{1}{\sqrt{7}}$					$\frac{1}{2\sqrt{35}}$							$-\frac{1}{2}$		$-\frac{1}{\sqrt{15}}$
X Y Y X							$-\frac{1}{\sqrt{6}}$		$\frac{1}{\sqrt{5}}$					$\frac{1}{\sqrt{10}}$	$\frac{1}{\sqrt{7}}$					$\frac{1}{2\sqrt{35}}$							$-\frac{1}{2}$		$-\frac{1}{\sqrt{15}}$
X Y Y Z										$-\frac{1}{\sqrt{2}}$						$-\frac{3}{\sqrt{42}}$					$-\frac{3}{\sqrt{28}}$				$\frac{1}{2\sqrt{7}}$				
X Y Z Y										$\frac{1}{\sqrt{2}}$						$-\frac{3}{\sqrt{42}}$					$-\frac{1}{\sqrt{28}}$				$\frac{1}{2\sqrt{7}}$				
X Y Z X											$\frac{1}{\sqrt{2}}$						$\frac{3}{\sqrt{42}}$					$\frac{1}{\sqrt{28}}$				$-\frac{1}{2\sqrt{7}}$			
X Y X Z											$-\frac{1}{\sqrt{2}}$						$\frac{3}{\sqrt{42}}$					$\frac{1}{\sqrt{28}}$				$-\frac{1}{2\sqrt{7}}$			
Y Z Y Z							$\frac{1}{\sqrt{6}}$		$\frac{1}{2\sqrt{5}}$				$-\frac{1}{2}$	$\frac{1}{\sqrt{10}}$	$\frac{-1}{2\sqrt{7}}$			$\frac{3}{2\sqrt{21}}$		$-\frac{2}{\sqrt{35}}$			$-\frac{1}{\sqrt{7}}$						$-\frac{1}{\sqrt{15}}$
Y Z Z Y							$-\frac{1}{\sqrt{6}}$		$-\frac{1}{2\sqrt{5}}$				$\frac{1}{2}$	$\frac{1}{\sqrt{10}}$	$-\frac{1}{2\sqrt{7}}$			$\frac{3}{2\sqrt{21}}$		$-\frac{2}{\sqrt{35}}$			$-\frac{1}{\sqrt{7}}$						$-\frac{1}{\sqrt{15}}$
Y Z Z X												$\frac{1}{\sqrt{2}}$						$\frac{3}{\sqrt{42}}$					$-\frac{2}{\sqrt{14}}$						
Y Z X Z												$-\frac{1}{\sqrt{2}}$						$\frac{3}{\sqrt{42}}$					$-\frac{2}{\sqrt{14}}$						
Z X Z X							$\frac{1}{\sqrt{6}}$		$\frac{1}{2\sqrt{5}}$				$\frac{1}{2}$	$\frac{1}{\sqrt{10}}$	$-\frac{1}{2\sqrt{7}}$			$-\frac{3}{2\sqrt{21}}$		$-\frac{2}{\sqrt{35}}$			$\frac{1}{\sqrt{7}}$						$-\frac{1}{\sqrt{15}}$
Z X X Z							$-\frac{1}{\sqrt{6}}$		$-\frac{1}{2\sqrt{5}}$				$-\frac{1}{2}$	$\frac{1}{\sqrt{10}}$	$-\frac{1}{2\sqrt{7}}$			$-\frac{3}{2\sqrt{21}}$		$-\frac{2}{\sqrt{35}}$			$\frac{1}{\sqrt{7}}$						$-\frac{1}{\sqrt{15}}$

Table 2 Transformation from irreducible spectra in the point group basis to experimental spectra. Row labels indicate the choice of primitive (i.e. geometrically independent) experimental arrangements made for the purposes of this paper; there is a considerable degree of arbitrariness in this choice, and the relations between the various experimental arrangements (table 3 of the main paper) are repeated here for convenience. The group theoretical labels use a notation defined in Churcher and Stedman (1981).

μ	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1
r	0	0	0	0	1	1	1	2	2	3	4	0	0	1	2	2	3
r′	0	1	2	3	1	2	3	2	3	3	4	0	1	1	2	3	3
β																	
XX	$\frac{1}{3}$	$\frac{-1}{3}$	-	$\frac{-1}{\sqrt{3}}$	$\frac{1}{6}$	-	$\frac{1}{\sqrt{6}}$	-	-	$\frac{1}{2}$	-	-	-	-	-	-	-
YY	$\frac{1}{3}$	$\frac{-1}{3}$	-	$\frac{1}{\sqrt{3}}$	$\frac{1}{6}$	-	$\frac{-1}{\sqrt{6}}$	-	-	$\frac{1}{2}$	-	-	-	-	-	-	-
ZZ	$\frac{1}{3}$	$\frac{2}{3}$	-	-	$\frac{2}{3}$	-	-	-	-	-	-	-	-	-	-	-	-
XY	-	-	-	-	-	-	-	$\frac{1}{2}$	-	-	$\frac{1}{2}$	-	-	-	-	-	-
XZ	-	-	-	-	-	-	-	-	-	-	-	$\frac{1}{2}$	-	-	$\frac{1}{2}$	-	-
YZ	-	-	-	-	-	-	-	-	-	-	-	-	-	$\frac{1}{2}$	-	-	$\frac{1}{2}$
XF	$\frac{1}{6}$	$\frac{-1}{6}$	$\frac{-1}{\sqrt{12}}$	$\frac{-1}{\sqrt{12}}$	$\frac{1}{12}$	$\frac{1}{2\sqrt{6}}$	$\frac{1}{2\sqrt{6}}$	$\frac{1}{4}$	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{4}$	$\frac{1}{4}$	-	-	-	-	-	-
YF	$\frac{1}{6}$	$\frac{-1}{6}$	$\frac{-1}{\sqrt{12}}$	$\frac{1}{\sqrt{12}}$	$\frac{1}{12}$	$\frac{1}{2\sqrt{6}}$	$\frac{-1}{2\sqrt{6}}$	$\frac{1}{4}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{4}$	$\frac{1}{4}$	-	-	-	-	-	-
EE	$\frac{1}{3}$	$\frac{1}{6}$	-	$\frac{-1}{\sqrt{12}}$	$\frac{1}{24}$	-	$\frac{-1}{4\sqrt{6}}$	-	-	$\frac{1}{8}$	-	$\frac{1}{2}$	-	-	-	-	-
HH	-	-	-	-	$\frac{3}{8}$	-	$\frac{3}{4\sqrt{6}}$	-	-	$\frac{1}{8}$	-	$\frac{1}{2}$	-	-	-	-	-
FF	$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{-1}{\sqrt{3}}$	-	$\frac{1}{6}$	$\frac{1}{\sqrt{6}}$	-	$\frac{1}{2}$	-	-	-	-	-	-	-	-	-
II	-	-	-	-	-	-	-	$\frac{1}{2}$	-	$\frac{1}{2}$	-	-	-	-	-	-	-
DD	$\frac{1}{3}$	$\frac{1}{6}$	-	$\frac{1}{\sqrt{12}}$	$\frac{1}{24}$	-	$\frac{1}{4\sqrt{6}}$	-	-	$\frac{1}{8}$	-	-	-	$\frac{1}{2}$	-	-	-
GG	-	-	-	-	$\frac{3}{8}$	-	$\frac{-3}{4\sqrt{6}}$	-	-	$\frac{1}{8}$	-	-	-	$\frac{1}{2}$	-	-	-
ZF	-	-	-	-	-	-	-	-	-	-	-	$\frac{1}{4}$	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{4}$
DE	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{-1}{2\sqrt{12}}$	-	$\frac{1}{6}$	$\frac{-1}{2\sqrt{6}}$	-	$\frac{1}{8}$	-	-	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{-1}{4\sqrt{2}}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{4\sqrt{2}}$	$\frac{1}{8}$
GH	$\frac{1}{12}$	$\frac{1}{6}$	$\frac{1}{2\sqrt{12}}$	-	$\frac{1}{6}$	$\frac{1}{2\sqrt{6}}$	-	$\frac{1}{8}$	-	-	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{-1}{4\sqrt{2}}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{4\sqrt{2}}$	$\frac{1}{8}$

XE = $\frac{1}{2}$(XX + XZ) ZE = $\frac{1}{2}$(XZ + ZZ)

XD = $\frac{1}{2}$(XY + XZ) ZD = $\frac{1}{2}$(ZZ + YZ)

YE = $\frac{1}{2}$(XY + YZ) EF = $\frac{1}{2}$(ZF + XF)

YD = $\frac{1}{2}$(YY + YZ) DF = $\frac{1}{2}$(YF + ZF)

GI = $\frac{1}{4}$(XY + YY + XZ + YZ) HI = $\frac{1}{4}$(XX + XY + XZ + YZ)

C_3 , C_{3i}

β \ μ	0	0	0	0	1	1	1	1	1
r	0	0	1	2	0	0	0	1	2
r′	0	1	1	2	0	1+	1−	1	2
XX	$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{1}{6}$	-	$\frac{1}{2\sqrt{2}}$	-	-	-	-
ZZ	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	-	-	-	-	-	-
XY	-	-	-	$\frac{1}{2}$	$\frac{1}{2\sqrt{2}}$	-	-	-	-
XZ	-	-	-	-	-	-	-	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$
HH	-	-	$\frac{3}{8}$	-	$\frac{1}{8\sqrt{2}}$	-	-	$\frac{1}{2\sqrt{2}}$	-
II	-	-	-	-	$1/\sqrt{2}$	-	-	-	-
DD	$\frac{1}{3}$	$\frac{1}{6}$	$\frac{1}{24}$	-	$\frac{1}{8\sqrt{2}}$	-	$\frac{-1}{4}$	$\frac{1}{2\sqrt{2}}$	-
XD	-	-	-	$\frac{1}{4}$	$\frac{1}{4\sqrt{2}}$	-	$\frac{1}{4}$	$\frac{1}{4\sqrt{2}}$	$\frac{1}{4\sqrt{2}}$
YE	-	-	-	$\frac{1}{4}$	$\frac{1}{4\sqrt{2}}$	$\frac{-1}{4}$	-	$\frac{1}{4\sqrt{2}}$	$\frac{1}{4\sqrt{2}}$

$XF = YF = \frac{1}{2}(XX + XY)$

$ZE = ZD = \frac{1}{2}(ZZ + XZ)$

$XE = \frac{1}{2}(XX - 2YE + XY + 2XZ)$

$EF = \frac{1}{4}(XX + 4XD - XY)$

$DE = \frac{1}{4}(ZZ + 2XD + 2YE - XY)$

$DF = \frac{1}{4}(XX + 4YE - XY)$

$YD = \frac{1}{2}(XX - 2XD + XY + 2XZ)$

$GH = \frac{1}{4}(ZZ + 2XZ + XY)$

$GI = HI = \frac{1}{4}(XX + 2XZ + XY)$

$EE = DD - YE + XD$

$YY = FF = XX$, $YZ = ZF = XZ$

$GG = HH$

C_4 , C_{4h} , S_4

β \ μ	0	0	0	0	2	2	2	1	1
r	0	0	1	2	0	0	1	0	1
r′	0	1	1	2	0	1	1	0	1
XX	$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{1}{6}$	-	$\frac{1}{2}$	-	-	-	-
ZZ	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	-	-	-	-	-	-
XY	-	-	-	$\frac{1}{2}$	-	-	$\frac{1}{2}$	-	-
XZ	-	-	-	-	-	-	-	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$
XF	$\frac{1}{6}$	$\frac{-1}{6}$	$\frac{1}{12}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{4}$	-	-
EE	$\frac{1}{3}$	$\frac{1}{6}$	$\frac{1}{24}$	-	$\frac{1}{8}$	-	-	$\frac{1}{2\sqrt{2}}$	-
HH	-	-	$\frac{3}{8}$	-	$\frac{1}{8}$	-	-	$\frac{1}{2\sqrt{2}}$	-
FF	$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{1}{6}$	-	-	-	$\frac{1}{2}$	-	-
II	-	-	-	-	$\frac{1}{2}$	-	$\frac{1}{2}$	-	-

$XE = YD = \frac{1}{2}(XX + XZ)$

$XD = YE = \frac{1}{2}(XY + XZ)$

$ZE = ZD = \frac{1}{2}(ZZ + XZ)$

$EF = \frac{1}{2}(XZ + XF)$

$DF = \frac{1}{2}(XZ + YF)$

$DE = GH = \frac{1}{4}(ZZ + XY + 2XZ)$

$HI = GI = \frac{1}{4}(XX + XY + 2XZ)$

$YF = XX + XY - XF$

$DD = EE$, $YY = XX$

$GG = HH$, $YZ = ZF = XZ$

C_6, C_{6h}, C_{3h} (D_6, D_{3h}, D_{6h}, C_{6v})

	μ	0	0	0	2	1	1	0	$\tilde{0}$
	r	0	0	1	0	0	1	2	0
	r′	0	1	1	0	0	1	2	0
β									
XX		$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{6}$	$\frac{1}{2\sqrt{2}}$	-	-	-	
ZZ		$\frac{1}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	-	-	-	-	
XY		-	-	-	$\frac{1}{2\sqrt{2}}$	-	-	$\frac{1}{2}$	○
XZ		-	-	-	-	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	-	
EE		$\frac{1}{3}$	$\frac{-1}{6}$	$\frac{1}{24}$	$\frac{1}{8\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	-	-	
HH		-	-	$\frac{3}{8}$	$\frac{1}{8\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	-	-	
II		-	-	-	$\frac{1}{\sqrt{2}}$	-	-	-	

$XF = YF = \frac{1}{2}(XX + XY)$

$XE = YD = \frac{1}{2}(XX + XZ)$

$XD = YE = \frac{1}{2}(XY + XZ)$

$ZE = ZD = \frac{1}{2}(ZZ + XZ)$

$DE = GH = \frac{1}{4}(ZZ + XY + 2XZ)$

$EF = DF = HI = GI = \frac{1}{4}(XX + XY + 2XZ)$

$DD = EE$, $GG = HH$

$XZ = ZF = XZ$

$YY = FF = XX$

D_2, D_{2h}, C_{2v}

	μ	0	0	0	0	0	0	$\tilde{0}$	$\tilde{0}$	1	1	$\tilde{1}$	$\tilde{1}$
	r	0	0	0	1	1	2	0	1	0	1	0	1
	r′	0	1	2	1	2	2	0	1	0	1	0	1
β													
XX		$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{-1}{\sqrt{3}}$	$\frac{1}{6}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{2}$	-	-	-	-	-	-
YY		$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{6}$	$\frac{-1}{\sqrt{6}}$	$\frac{1}{2}$	-	-	-	-	-	-
ZZ		$\frac{1}{3}$	$\frac{2}{3}$	-	$\frac{2}{3}$	-	-	-	-	-	-	-	-
XY		-	-	-	-	-	-	$\frac{1}{2}$	$\frac{1}{2}$	-	-	-	-
XZ		-	-	-	-	-	-	-	-	$\frac{1}{2}$	$\frac{1}{2}$	-	-
YZ		-	-	-	-	-	-	-	-	-	-	$\frac{1}{2}$	$\frac{1}{2}$
EE		$\frac{1}{3}$	$\frac{1}{6}$	$\frac{-1}{\sqrt{2}}$	$\frac{1}{24}$	$\frac{-1}{4\sqrt{6}}$	$\frac{1}{8}$	-	-	$\frac{1}{2}$	-	-	-
HH		-	-	-	$\frac{3}{8}$	$\frac{3}{4\sqrt{6}}$	$\frac{1}{8}$	-	-	$\frac{1}{2}$	-	-	-
FF		$\frac{1}{3}$	$\frac{-1}{3}$	-	$\frac{1}{6}$	-	-	$\frac{1}{2}$	-	-	-	-	-
II		-	-	-	-	-	$\frac{1}{2}$	$\frac{1}{2}$	-	-	-	-	-
DD		$\frac{1}{3}$	$\frac{1}{6}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{24}$	$\frac{1}{4\sqrt{6}}$	$\frac{1}{8}$	-	-	-	-	$\frac{1}{2}$	-
GG		-	-	-	$\frac{3}{8}$	$\frac{-3}{4\sqrt{6}}$	$\frac{1}{8}$	-	-	-	-	$\frac{1}{2}$	

$XF = \frac{1}{2}(XX + XY)$ $\quad$ $ZF = \frac{1}{2}(XZ + YZ)$

$XE = \frac{1}{2}(XX + XZ)$ $\quad$ $ZE = \frac{1}{2}(ZZ + XZ)$

$XD = \frac{1}{2}(XY + XZ)$ $\quad$ $ZD = \frac{1}{2}(ZZ + YZ)$

$YF = \frac{1}{2}(YY + XY)$ $\quad$ $EF = HI = \frac{1}{4}(YY + XY + XZ + YZ)$

$YE = \frac{1}{2}(XY + YZ)$ $\quad$ $DF = GI = \frac{1}{4}(XX + XY + XZ + YZ)$

$YD = \frac{1}{2}(YY + YZ)$ $\quad$ $DE = GH = \frac{1}{4}(ZZ + XY + XZ + YZ)$

D_3, C_{3v}, D_{3d}

	μ	0	0	0	1	1	1	1	$\tilde{0}$
	r	0	0	1	0	0	1	2	0
β	r′	0	1	1	0	1	1	2	0
XX		$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{1}{6}$	$\frac{1}{2\sqrt{2}}$	-	-	-	-
ZZ		$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	-	-	-	-	-
XY		-	-	-	$\frac{1}{2\sqrt{2}}$	-	-	-	$\frac{1}{2}$
XZ		-	-	-	-	-	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	-
HH		-	-	$\frac{3}{8}$	$\frac{1}{8\sqrt{2}}$	-	$\frac{1}{2\sqrt{2}}$	-	-
II		-	-	-	$1/4\sqrt{2}$	-	-	-	-
DD		$\frac{1}{3}$	$\frac{1}{6}$	$\frac{1}{24}$	$\frac{1}{8\sqrt{2}}$	-	$\frac{1}{2\sqrt{2}}$	-	-
YE		-	-	-	$\frac{1}{4\sqrt{2}}$	$\frac{-1}{4}$	$\frac{1}{4\sqrt{2}}$	$\frac{1}{4\sqrt{2}}$	$\frac{1}{4}$

$XF = YF = \frac{1}{2}(XX + XY)$

$ZE = ZD = \frac{1}{2}(ZZ + XZ)$

$YD = \frac{1}{2}(XX + XZ)$

$XD = \frac{1}{2}(XY + XZ)$

$YY = FF = XX$

$YZ = ZF = XZ$

$GG = HH$

$XE = \frac{1}{2}(XX - 2YE + XY + 2XZ)$

$EE = \frac{1}{2}(2DD - 2YE + XY + XZ)$

$DE = \frac{1}{4}(ZZ + 2YE + XZ)$

$GH = \frac{1}{4}(ZZ + XY + 2XZ)$

$EF = GI = HI = \frac{1}{4}(XX + XY + 2XZ)$

$DF = \frac{1}{4}(XX + 4YE - XY)$

D_4, D_{2d}, D_{4h}, C_{4v}

	μ	0	0	0	2	$\tilde{2}$	1	1	$\tilde{0}$
	r	0	0	1	0	0	0	1	0
β	r′	0	1	1	0	0	0	1	0
XX		$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{1}{6}$	$\frac{1}{2}$	-	-	-	-
ZZ		$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	-	-	-	-	-
XY		-	-	-	-	$\frac{1}{2}$	-	-	$\frac{1}{2}$
XZ		-	-	-	-	-	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	-
EE		$\frac{1}{3}$	$\frac{1}{6}$	$\frac{1}{24}$	$\frac{1}{8}$	-	$\frac{1}{2\sqrt{2}}$	-	-
HH		-	-	$\frac{3}{8}$	$\frac{1}{8}$	-	$\frac{1}{2\sqrt{2}}$	-	-
FF		$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{1}{6}$	-	$\frac{1}{2}$	-	-	-
II		-	-	-	$\frac{1}{2}$	$\frac{1}{2}$	-	-	-

$XF = YF = \frac{1}{2}(XX + XY)$

$XE = YD = \frac{1}{2}(XX + XZ)$

$XD = YE = \frac{1}{2}(XY + XZ)$

$ZE = ZD = \frac{1}{2}(ZZ + XZ)$

$YZ = ZF = XZ$

$DD = EE$, $GG = HH$

$XX = YY$

$DE = GH = \frac{1}{4}(ZZ + XY + 2XZ)$

$EF = DF = HI = GI = \frac{1}{4}(XX + XY + 2XZ)$

C_2, C_s, C_{2h} irreducible spectra in a point group basis.

μrr′ \ β	XX	YY	ZZ	XY	XZ	YZ	XF	YF	EE	HH	FF	II	DD	GG	ZF	DE	GH
000	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{2}{3}$	-	-	$\frac{-2}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{-2}{3}$	-	-	-
001	$\frac{-2}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{-2}{3}$	-	-	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{-1}{3}$	-	-	-
002	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	$\frac{2}{\sqrt{3}}$	-	-	$\frac{-2}{\sqrt{3}}$	$\frac{-2}{\sqrt{3}}$	-	-	-	-	-	-	-	$\frac{-2}{\sqrt{3}}$	$\frac{2}{\sqrt{3}}$
003	$\frac{-1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	-	-	-	-	-	$\frac{-1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	-	$\frac{1}{\sqrt{3}}$	$\frac{-1}{\sqrt{3}}$	-	-	-
011	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	-	-	$\frac{-1}{3}$	$\frac{-1}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	-	-	-
012	$\frac{-1}{\sqrt{6}}$	$\frac{-1}{\sqrt{6}}$	-	$\frac{-2}{\sqrt{6}}$	-	-	$\frac{2}{\sqrt{6}}$	$\frac{2}{\sqrt{6}}$	-	-	-	-	-	-	-	$\frac{-4}{\sqrt{6}}$	$\frac{4}{\sqrt{6}}$
013	$\frac{1}{\sqrt{6}}$	$\frac{-1}{\sqrt{6}}$	-	-	-	-	-	-	$\frac{-2}{\sqrt{6}}$	$\frac{2}{\sqrt{6}}$	-	-	$\frac{2}{\sqrt{6}}$	$\frac{-2}{\sqrt{6}}$	-	-	-
022	-	-	-	1	-	-	-1	-1	-	-	1	1	-	-	-	-	-
023	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	-	-	$-\sqrt{2}$	$\sqrt{2}$	-	-	-	-	-	-	-	-	-
033	-	-	-	-1	-	-	1	1	-	-	-1	1	-	-	-	-	-
044	-	-	-	1	-	-	1	1	-	-	-1	-1	-	-	-	-	-
100	$\frac{-1}{2}$	-	$\frac{-1}{2}$	-	-	-	-	-	1	1	-	-	-	-	-	-	-
101	-	-	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	$\sqrt{2}$	$\sqrt{2}$	-	-	-	-	-	-	-	-	$-\sqrt{2}$	$-\sqrt{2}$	$-\sqrt{2}$
111	-	$\frac{-1}{2}$	$\frac{-1}{2}$	-	-	-	-	-	-	-	-	-	1	1	-	-	-
122	$\frac{1}{2}$	-	$\frac{1}{2}$	-	2	-	-	-	-1	-1	-	-	-	-	-	-	-
123	-	-	$\frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	-	-	-	-	-	-	-	-	$-\sqrt{2}$	$\sqrt{2}$	$\sqrt{2}$
133	-	$\frac{1}{2}$	$\frac{1}{2}$	-	-	2	-	-	-	-	-	-	-1	-1	-	-	-

O, O_h, T_d (T, T_h)

	β: XX	XY	HH	DD
μ 0 2 T(1) 1(1)	$\frac{1}{3}$	$\frac{\sqrt{2}}{3}$	-	-
r 0 0 0(0) 0(1)	-	-	$\frac{1}{2\sqrt{2}}$	$\frac{1}{6\sqrt{2}}$
r′ 0 0 0(0) 0(1)	-	$\frac{1}{2\sqrt{3}}$	$\frac{1}{2\sqrt{3}}$	$\frac{1}{2\sqrt{3}}$
	-	$\frac{1}{2\sqrt{3}}$	-	-

YY = ZZ = XX

EE = FF = DD

GG = HH = II

XZ = XD = ZF = YZ = YE = XY

XF = XE = YF = YD = ZE = ZD

$= \frac{1}{2}$ (XX + XY)

EF = DF = HI = GI = DE = GH

$= \frac{1}{4}$ (XX + 3XY)

K, R_3

	β: XX	XY	HH
μ 0 1 2	$\frac{1}{3}$	-	$\frac{2}{3\sqrt{5}}$
r 0 0 0	-	$\frac{1}{2\sqrt{3}}$	$\frac{1}{2\sqrt{5}}$
r′ 0 0 0	-	-	$\frac{1}{\sqrt{5}}$

XX = YY = ZZ = DD = EE = FF

GG = HH = II

XZ = YZ = YE = ZF = XD = XY

XF = XE = YF = YD = ZE = ZD

$= \frac{1}{2}$ (XX + XY)

EF = DF = DE = GH = GI = HI

$= \frac{1}{2}$ (XX + 3XY)

C_3, C_{3i}

μrr′ \ β	XX	ZZ	XY	XZ	HH	II	DD	XD	YE
000	$\frac{4}{3}$	$\frac{1}{3}$	$\frac{-2}{3}$	$\frac{-2}{3}$	$\frac{-4}{3}$	$\frac{-2}{3}$	$\frac{4}{3}$	$\frac{4}{3}$	-
001	$\frac{-4}{3}$	$\frac{2}{3}$	$\frac{-1}{3}$	$\frac{-1}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	-
011	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{4}{3}$	$\frac{-1}{3}$	$\frac{-4}{3}$	$\frac{-4}{3}$	-
022	-	-	2	-	-	-1	-	-	-
100	-	-	-	-	-	$\sqrt{2}$	-	-	-
101	-	-	2	2	-	-	-	-	-4
110	-	-	-2	-2	-	-	-	4	-
111	$\frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	$\sqrt{2}$	-	$\sqrt{2}$	$\sqrt{2}$	-
122	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	$\frac{5}{\sqrt{2}}$	$\sqrt{2}$	-	$\sqrt{2}$	$-\sqrt{2}$	-

C_4, C_{4h}, S_4

μrr′ \ β	XX	ZZ	XY	XZ	XF	EE	HH	FF	II
000	$\frac{2}{3}$	$\frac{1}{3}$	-	-	-	$\frac{4}{3}$	$\frac{-4}{3}$	$\frac{2}{3}$	$\frac{-2}{3}$
001	$\frac{-2}{3}$	$\frac{2}{3}$	-	-	-	$\frac{2}{3}$	$\frac{-2}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$
011	$\frac{1}{3}$	$\frac{2}{3}$	-	-	-	$\frac{-4}{3}$	$\frac{4}{3}$	$\frac{1}{3}$	$\frac{-1}{3}$
022	1	-	2	-	-	-	-	-1	-1
200	1	-	-	-	-	-	-	-1	1
201	$\sqrt{2}$	-	$\sqrt{2}$	-	$-2\sqrt{2}$	-	-	-	-
211	-1	-	-	-	-	-	-	1	1
100	$\frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	-	$\sqrt{2}$	$\sqrt{2}$	-	-
111	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-	$2\sqrt{2}$	-	$-\sqrt{2}$	$-\sqrt{2}$	-	-

μrr′ \ β	XX	ZZ	XY	XZ	EE	HH	II
000	$\frac{4}{3}$	$\frac{1}{3}$	-	-	$\frac{4}{3}$	$\frac{-4}{3}$	$\frac{-2}{3}$
001	$\frac{4}{3}$	$\frac{-2}{3}$	-	-	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{-2}{3}$
011	$\frac{2}{3}$	$\frac{2}{3}$	-	-	$\frac{-4}{3}$	$\frac{4}{3}$	$\frac{-1}{3}$
200	-	-	-	-	-	-	$\sqrt{2}$
100	$\frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	$\sqrt{2}$	$\sqrt{2}$	-
111	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-	$2\sqrt{2}$	$-\sqrt{2}$	$-\sqrt{2}$	-
~(000)022	-	-	2	-	-	-	-1

D_2, D_{2h}, C_{2v}

μrr′ \ β	XX	YY	ZZ	XY	XZ	YZ	EE	HH	FF	II	DD	GG
000	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	-	-	-	$\frac{2}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{-2}{3}$
001	$\frac{-1}{3}$	$\frac{-1}{3}$	$\frac{2}{3}$	-	-	-	$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{-1}{3}$
002	$\frac{-1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	-	-	-	$\frac{-1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	-	-	$\frac{1}{\sqrt{3}}$	$\frac{-1}{\sqrt{3}}$
011	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{2}{3}$	-	-	-	$\frac{-2}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$
012	$\frac{1}{\sqrt{6}}$	$\frac{-1}{\sqrt{6}}$	-	-	-	-	$\frac{-2}{\sqrt{6}}$	$\frac{2}{\sqrt{6}}$	-	-	$\frac{2}{\sqrt{6}}$	$\frac{-2}{\sqrt{6}}$
022	$\frac{1}{2}$	$\frac{1}{2}$	-	-	-	-	-	-	-1	1	-	-
~000	$\frac{-1}{2}$	$\frac{-1}{2}$	-	-	-	-	-	-	1	1	-	-
~011	$\frac{1}{2}$	$\frac{1}{2}$	-	2	-	-	-	-	-1	-1	-	-
100	$\frac{-1}{2}$	-	$\frac{-1}{2}$	-	-	-	1	1	-	-	-	-
111	$\frac{1}{2}$	-	$\frac{1}{2}$	-	2	-	-1	-1	-	-	-	-
~100	-	$\frac{-1}{2}$	$\frac{-1}{2}$	-	-	-	-	-	-	-	1	1
~111	-	$\frac{1}{2}$	$\frac{1}{2}$	-	-	2	-	-	-	-	-1	-1

μrr′ \ β	XX	ZZ	XY	XZ	HH	II	DD	YE
000	$\frac{4}{3}$	$\frac{1}{3}$	-	-	$\frac{-4}{3}$	$\frac{-2}{3}$	$\frac{4}{3}$	-
001	$-\frac{4}{3}$	$\frac{2}{3}$	-	-	$-\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	-
011	$\frac{2}{3}$	$\frac{2}{3}$	-	-	$\frac{4}{3}$	$\frac{-1}{3}$	$\frac{-4}{3}$	-
100	-	-	-	-	-	$\sqrt{2}$	-	-
101	-	-	2	2	-	-	-	-4
111	$\frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	$\sqrt{2}$	-	$\sqrt{2}$	-
122	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-	$2\sqrt{2}$	$-\sqrt{2}$	-	$-\sqrt{2}$	-
~000	-	-	2	-	-	-1	-	-

$D_4, D_{2d}, D_{4h}, C_{4v}$

μrr′ \ β	XX	ZZ	XY	XZ	EE	HH	FF	II
000	$\frac{2}{3}$	$\frac{1}{3}$	-	-	$\frac{4}{3}$	$\frac{-4}{3}$	$\frac{2}{3}$	$\frac{-2}{3}$
001	$-\frac{2}{3}$	$\frac{2}{3}$	-	-	$\frac{2}{3}$	$-\frac{2}{3}$	$-\frac{2}{3}$	$\frac{2}{3}$
011	$-\frac{1}{3}$	$\frac{2}{3}$	-	-	$\frac{-4}{3}$	$\frac{4}{3}$	$\frac{1}{3}$	$\frac{-1}{3}$
200	1	-	-	-	-	-	-1	1
~200	-1	-	-	-	-	-	1	1
100	$\frac{-1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	$\sqrt{2}$	$\sqrt{2}$	-	-
111	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-	$2\sqrt{2}$	$-\sqrt{2}$	$-\sqrt{2}$	-	-
~000	1	-	2	-	-	-	-1	-1

$O, O_h, T_d, (T, T_h)$

μrr′ \ β	XX	XY	HH	DD
000	1	-	-2	2
200	$\sqrt{2}$	-	$\sqrt{2}$	$-\sqrt{2}$
(100) ~100	$-\sqrt{3}$	-	$\sqrt{3}$	$\sqrt{3}$
(111) 100	$\sqrt{3}$	$\sqrt{3}$	$-\sqrt{3}$	$-\sqrt{3}$

K, R_3

μrr′ \ β	XX	XY	HH
000	3	-	-2
100	-	$2\sqrt{3}$	$-\sqrt{3}$
200	-	-	$\sqrt{5}$

Table 4. Connection between cartesian and point group labels i.e. the transformation $T^{++}_{\rho\rho'\sigma\sigma'}{}^{\mu\, rr'\xi}$ from $c^{++}_{\mu rr'\xi}$ to $c^{++}_{\rho\rho'\sigma\sigma'}$. The inverse is obtained by unitarity. Below each table we give the symmetries between the labels $\rho\rho'\sigma\sigma'$ applicable in each point group (label choices not listed here or in the table vanish in the group considered), and also symmetrised versions used in defining N^{++} independent row labels. The combinations

$$a_n = \tfrac{1}{2}\left[(1/\sqrt{2})(xxxx + yyzz) + \phi_n\, xxyy + \psi_n\, xyxy - \phi_n\,\psi_n\, xyyx\right]$$

appears in several groups, where $\phi_n = +,+,-$ and $\psi_n = +,-,+$ for $n = 1,2,3$ respectively.

$\rho\rho'\sigma\sigma'$	μ 0	0	0	0	0	0	0	0	0	0	0
	r 0	0	0	0	1	1	1	2	2	3	4
	r′ 0	1	2	3	1	2	3	2	3	3	4
xxxx	$\frac{1}{3}$	$\frac{-1}{3}$	-	$\frac{-1}{\sqrt{3}}$	$\frac{1}{6}$	-	$\frac{1}{\sqrt{6}}$	-	-	$\frac{1}{2}$	-
xxyy	$\frac{2}{3\sqrt{2}}$	$\frac{-2}{3\sqrt{2}}$	-	-	$\frac{1}{3\sqrt{2}}$	-	-	-	-	$\frac{-1}{\sqrt{2}}$	-
xxzz	$\frac{2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	-	$\frac{-1}{\sqrt{6}}$	$\frac{-2}{3\sqrt{2}}$	-	$\frac{-1}{\sqrt{3}}$	-	-	-	-
xxxy	-	-	$\frac{-1}{\sqrt{3}}$	-	-	$\frac{1}{\sqrt{6}}$	-	-	$\frac{-1}{\sqrt{2}}$	-	-
yyyy	$\frac{1}{3}$	$\frac{-1}{3}$	-	$\frac{1}{\sqrt{3}}$	$\frac{1}{6}$	-	$\frac{-1}{\sqrt{6}}$	-	-	$\frac{1}{2}$	-
yyzz	$\frac{2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	-	$\frac{1}{\sqrt{6}}$	$\frac{-2}{3\sqrt{2}}$	-	$\frac{1}{\sqrt{3}}$	-	-	-	-
yyxy	-	-	$\frac{-1}{\sqrt{3}}$	-	-	$\frac{1}{\sqrt{6}}$	-	-	$\frac{1}{\sqrt{2}}$	-	-
zzzz	$\frac{1}{3}$	$\frac{2}{3}$	-	-	$\frac{2}{3}$	-	-	-	-	-	-
zzxy	-	-	$\frac{-1}{\sqrt{3}}$	-	-	$\frac{-2}{\sqrt{6}}$	-	-	-	-	-
xyxy	-	-	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	-	-	$\frac{1}{\sqrt{2}}$
xyyx	-	-	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	-	-	$\frac{-1}{\sqrt{2}}$

	μ 1	1	1	1	1	1
	r 0	0	1	2	2	3
	r′ 0	1	1	2	3	3
yzyz	-	-	$\frac{1}{\sqrt{2}}$	-	-	$\frac{1}{\sqrt{2}}$
yzzy	-	-	$\frac{1}{\sqrt{2}}$	-	-	$\frac{-1}{\sqrt{2}}$
yzzx	-	$\frac{-1}{\sqrt{2}}$	-	-	$\frac{1}{\sqrt{2}}$	-
yzxz	-	$\frac{-1}{\sqrt{2}}$	-	-	$\frac{-1}{\sqrt{2}}$	-
zxzx	$\frac{1}{\sqrt{2}}$	-	-	$\frac{1}{\sqrt{2}}$	-	-
zxxz	$\frac{1}{\sqrt{2}}$	-	-	$\frac{-1}{\sqrt{2}}$	-	-

Table 4 Page 2

C_3 , C_{3i}

$\rho\rho'\sigma\sigma'$	μ 0	0	0	0	1	1	1	1	1
	r 0	0	0	2	0	0_+	0_-	1	2
	r' 0	1	1	2	0	1^+	1^-	1	2
a_1	$\frac{2}{3\sqrt{2}}$	$\frac{-2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-	-	-	-	-
a_2	$\frac{2}{3\sqrt{2}}$	$\frac{-2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	-	-	-
zzzz	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	-	-	-	-	-	-
$xxzz^+$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{-2}{3}$	-	-	-	-	-	-
a_3	-	-	-	-	1	-	-	-	-
$xxzx^+$	-	-	-	-	-	1	-	-	-
$yyyz^+$	-	-	-	-	-	-	-1	-	-
$yzyz^+$	-	-	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$
$zxzx^+$	-	-	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$

$$xxzx^+ = \frac{1}{2}(xxzx - yyzx - xyyz - xyyz)$$
$$yyyz^+ = \frac{1}{2}(yyyz - xxyz - xyzx - xyxz)$$
$$yzyz^+ = \frac{1}{\sqrt{2}}(yzyz + yzzy)$$
$$zxzx^+ = \frac{1}{\sqrt{2}}(zxzx + zxxz)$$
$$xxzz^+ = \frac{1}{\sqrt{2}}(xxzz + yyzz)$$

YYYY = XXXX , YYZZ = XXZZ , XXYZ = XYZX = XYXZ = -(YYYZ) ,

ZXZX = YZYZ , ZXXZ = YZZY , YYZX = XYYZ = XYZY = -(XXZX) ,

XYYX = XXXX - XXYY - XYXY

Table 4 Page 3

C_4 , C_{4h} , S_4

$\rho\rho'\sigma\sigma'$	μ 0	0	0	0	2	2	2	1	1
	r 0	0	1	2	0	0	1	0	1
	r' 0	1	1	2	0	1	1	0	1
$xxxx^+$	$\frac{2}{3\sqrt{2}}$	$\frac{-2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	-	$\frac{1}{\sqrt{2}}$	-	-	-	-
xxyy	$\frac{2}{3\sqrt{2}}$	$\frac{-2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	-	$\frac{-1}{\sqrt{2}}$	-	-	-	-
$xxzz^+$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{-2}{3}$	-	-	-	-	-	-
zzzz	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	-	-	-	-	-	-
$xxxy^+$	-	-	-	-	-	-1	-	-	-
xyxy	-	-	-	$\frac{1}{\sqrt{2}}$	-	-	$\frac{1}{\sqrt{2}}$	-	-
xyyx	-	-	-	$\frac{-1}{\sqrt{2}}$	-	-	$\frac{1}{\sqrt{2}}$	-	-
$yzyz^+$	-	-	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$
$zxzx^+$	-	-	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$

$$xxxx^+ = \frac{1}{\sqrt{2}}(xxxx + yyyy)$$
$$xxzz^+ = \frac{1}{\sqrt{2}}(xxzz + yyzz)$$
$$xxxy^+ = \frac{1}{\sqrt{2}}(xxxy - yyxy)$$
$$yzyz^+ = \frac{1}{\sqrt{2}}(yzyz + yzzy)$$
$$zxzx^+ = \frac{1}{2}(zxzx + zxxz)$$

YYYY = XXXX

YYZZ = XXZZ

YYXY = - (XXXY)

ZXZX = YZYZ

ZXXZ = YZZY

C_6 , C_{6h} , C_{3h} (D_6 , C_{6v} , D_{3h} , D_{6h})

$\rho\rho'\sigma\sigma'$	μ r r′	0 0 0	0 0 1	0 1 1	0 2 2	(0 0 0)	2 0 0	1 0 1	1 1 1
a_1		$\frac{2}{3\sqrt{2}}$	$\frac{2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	$\frac{1}{\sqrt{2}}$		-	-	-
a_2		$\frac{2}{3\sqrt{2}}$	$\frac{2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$		-	-	-
zzzz		$\frac{1}{3}$	$\frac{-2}{3}$	$\frac{2}{3}$	-		-	-	-
$xxzz^+$		$\frac{2}{3}$	$\frac{-1}{3}$	$\frac{-2}{3}$	-		-	-	-
a_3		-	-	-	-		1	-	-
$yzyz^+$		-	-	-	-		-	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$
$zxzx^+$		-	-	-	-		-	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$

$$xxzz^+ = \frac{1}{\sqrt{2}}(xxzz + yyzz)$$

$$yzyz^+ = \frac{1}{\sqrt{2}}(yzyz + yzzy)$$

$$zxzx^+ = \frac{1}{\sqrt{2}}(zxzx + zxxz)$$

$$YYYY = XXXX \,, \quad YYZZ = XXZZ \,, \quad YZZY = ZXXZ$$

$$XYYX = XXXX - XXYY - XYXY \,, \quad ZXZX = YZYZ$$

D_2 , D_{2h} , C_{2v}

$\rho\rho'\sigma\sigma'$	μ r r′	0 0 0	0 0 1	0 0 2	0 1 1	0 1 2	0 2 2
xxxx		$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{-1}{\sqrt{3}}$	$\frac{1}{6}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{2}$
xxyy		$\frac{2}{3\sqrt{2}}$	$\frac{-2}{3\sqrt{2}}$	-	$\frac{1}{3\sqrt{2}}$	-	$\frac{-1}{\sqrt{2}}$
xxzz		$\frac{2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	$\frac{-1}{\sqrt{6}}$	$\frac{-2}{3\sqrt{2}}$	$\frac{-1}{\sqrt{3}}$	-
yyyy		$\frac{1}{3}$	$\frac{-1}{3}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{6}$	$\frac{-1}{\sqrt{6}}$	$\frac{1}{2}$
yyzz		$\frac{2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	$\frac{1}{\sqrt{6}}$	$\frac{-2}{3\sqrt{2}}$	$\frac{1}{\sqrt{3}}$	-
zzzz		$\frac{1}{3}$	$\frac{2}{3}$	-	$\frac{2}{3}$	-	-

$\rho\rho'\sigma\sigma'$	μ r r′	~ 0 0	~ 0 1	1 0 0	1 1 1	~ 1 0	~ 1 1
xyxy		$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-	-	-	-
xyyx		$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	-	-
yzyz		-	-	-	-	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$
yzzy		-	-	-	-	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$
zxzx		-	-	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-	-
zxxz		-	-	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-

D_3 , D_{3d} , C_{3v}

$\rho\rho'\sigma\sigma'$	μ r r' 0 0 0	0 0 1	0 1 1	1 0 0	1 0 1	1 1 1	1 2 2	$\tilde{0}$ 0 0 0
a_1	$\frac{2}{3\sqrt{2}}$	$\frac{-2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	-	-	-	-	$\frac{1}{\sqrt{2}}$
a_2	$\frac{2}{3\sqrt{2}}$	$\frac{-2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	-	-	-	-	$\frac{-1}{\sqrt{2}}$
$xxzz^+$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{-2}{3}$	-	-	-	-	-
zzzz	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	-	-	-	-	-
a_3	-	-	-	1	-	-	-	-
$xxzx^+$	-	-	-	-	1	-	-	-
$yzyz^+$	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-
$zxzx^+$	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-

$$xxzz^+ = \frac{1}{\sqrt{2}}(xxzz + yyzz) \qquad yzyz^+ = \frac{1}{\sqrt{2}}(yzyz + yzzy)$$

$$zxzx^+ = \frac{1}{\sqrt{2}}(zxzx + zxxz) \qquad xxzx^+ = \frac{1}{2}(xxzx - yyzx - xyyz - xyzy)$$

YYYY = XXXX,, YYZZ = XXZZ , ZXZX = YZYZ ,

ZXXZ = YZZY , XYYX = XXXX - XXYY - XYXY ,

YYZX = XYYZ = XYZY = -(XXZX)

D_4 , D_{4h} , C_{2v} , D_{2d}

$\rho\rho'\sigma\sigma'$	μ r r' 0 0 0	0 0 1	0 1 1	2 0 0	$\tilde{2}$ 0 0	1 0 0	1 1 1	$\tilde{1}$ 0 0
$xxxx^+$	$\frac{2}{3\sqrt{2}}$	$\frac{-2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-	-	-	-
xxyy	$\frac{2}{3\sqrt{2}}$	$\frac{-2}{3\sqrt{2}}$	$\frac{1}{3\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-	-	-	-
$xxzz^+$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{-2}{3}$	-	-	-	-	-
zzzz	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	-	-	-	-	-
xyxy	-	-	-	-	$\frac{1}{\sqrt{2}}$	-	-	$\frac{1}{\sqrt{2}}$
xyyx	-	-	-	-	$\frac{1}{\sqrt{2}}$	-	-	$\frac{-1}{\sqrt{2}}$
$yzyz^+$	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	-
$zxzx^+$	-	-	-	-	-	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	-

$$xxxx^+ = \frac{1}{\sqrt{2}}(xxxx + yyyy) \qquad xxzz^+ = \frac{1}{\sqrt{2}}(xxzz + yyzz)$$

$$yzyz^+ = \frac{1}{\sqrt{2}}(yzyz + yzzy) \qquad zxzx^+ = \frac{1}{\sqrt{2}}(zxzx + zxxz)$$

YYYY = XXXX , YYZZ = XXZZ ,

ZXZX = YZYZ , YZZY = ZXXZ .

$T_1 , T_{1h} , (0_1 , 0_{1h} , T_{1d})$

$\rho\rho'\sigma\sigma'$	μ r r′ 0 0 0	0 0 0	2 0 0	1 0 0 (1̃ 0 0)	1 1 1 (1 0 0)
$xxxx^+$		$\frac{1}{\sqrt{3}}$	$\frac{2}{\sqrt{6}}$	-	-
$xxyy^+$		$\frac{2}{\sqrt{6}}$	$\frac{-1}{\sqrt{3}}$	-	-
$xyxy^+$		-	-	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$
$xyyx^+$		-	-	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$

$$xxxx^+ = \frac{1}{\sqrt{3}} (xxxx + yyyy + zzzz)$$

$$xxyy^+ = \frac{1}{\sqrt{3}} (xxyy + yyzz + zzxx)$$

$$xyxy^+ = \frac{1}{\sqrt{3}} (xyxy + yzyz + zxzx)$$

$$xyyx^+ = \frac{1}{\sqrt{3}} (xyyx + yzzy + zxxz)$$

YYYY = ZZZZ = XXXX , XXYY = XXZZ = YYZZ

XYXY = YZYZ = ZXZX , XYYX = YZZY = ZXXZ

K_3 , R_3

$\rho\rho'\sigma\sigma'$	μ r r′ 0 0 0	0 0 0	1 0 0	2 0 0
b_1		$\frac{3}{\sqrt{15}}$	$\frac{2}{\sqrt{10}}$	-
b_2		$\frac{1}{\sqrt{15}} - \frac{2}{\sqrt{30}}$	$\frac{1}{\sqrt{5}} - \frac{1}{\sqrt{10}}$	$\frac{1}{\sqrt{3}} + \frac{1}{\sqrt{6}}$
b_3		$\frac{1}{\sqrt{15}} + \frac{2}{\sqrt{30}}$	$\frac{-1}{\sqrt{5}} - \frac{1}{\sqrt{10}}$	$\frac{1}{\sqrt{3}} - \frac{1}{\sqrt{6}}$

$$b_1 = \frac{1}{\sqrt{5}} (xxxx^+ + \sqrt{2}\ xxyy^+ + xyxy^+ - xyyx^+)$$

$$b_2 \quad \frac{1}{\sqrt{5}} (xxxx^+ - xxyy^+ + \sqrt{2}\ xyxy^+ + xyyx^+)$$

$$b_3 \quad \frac{1}{\sqrt{5}} (xxxx^+ + xxyy^+ - xyxy^+ + \sqrt{2}\ xyyx^+)$$

with $xxxx^+$ etc. as for T.

YYZZ = XXZZ = XXYY = XXXX - XYXY - XYYX

YYYY = ZZZZ = XXXX , ZXZX = YZYZ = XYXY ,

ZXXZ = YZZY = XYYX

Table 5. Transformation from cartesian to experimental spectra.

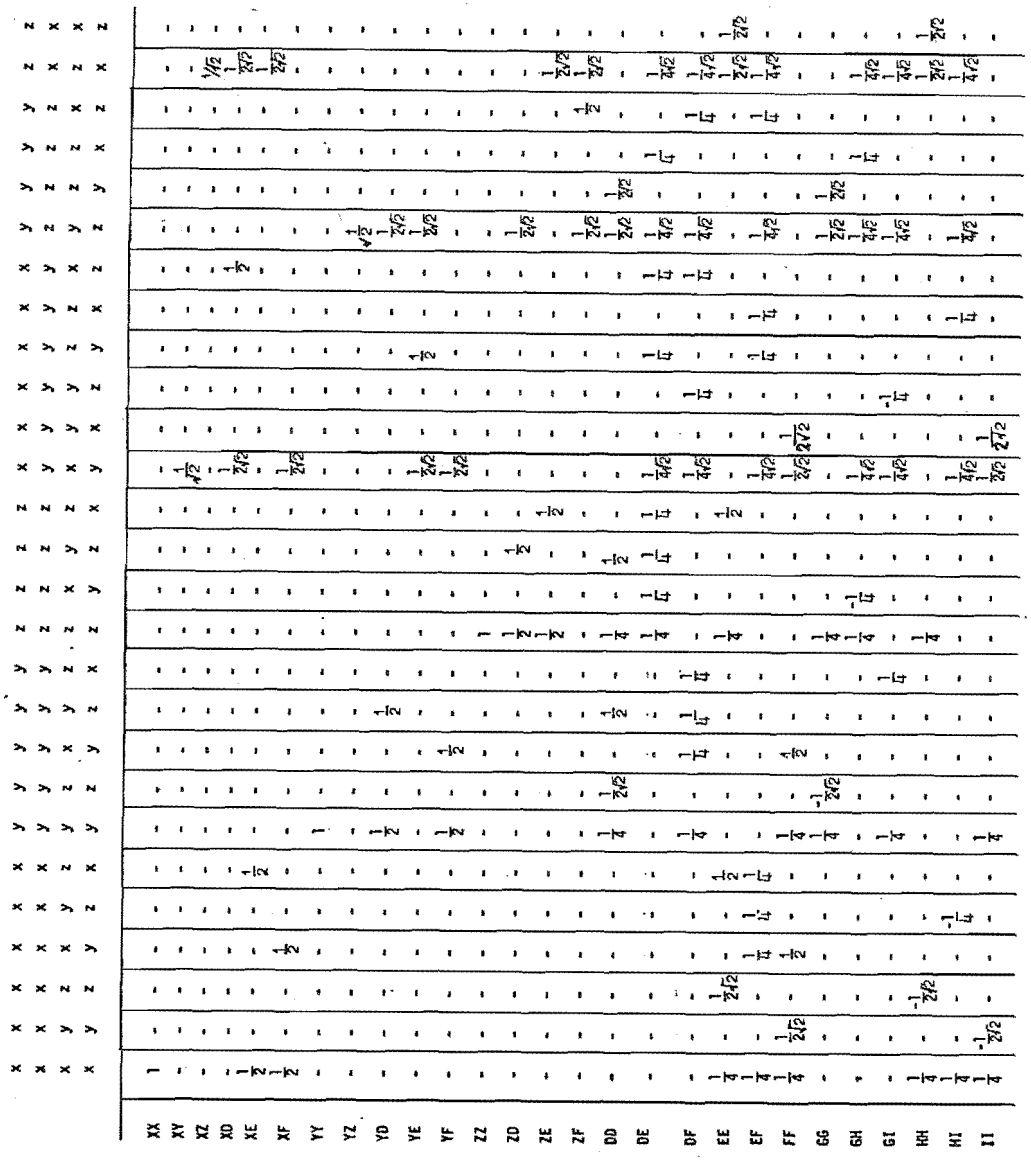

Table 6 Transformation from the irreducible spectra in the spherical basis to experimental spectra

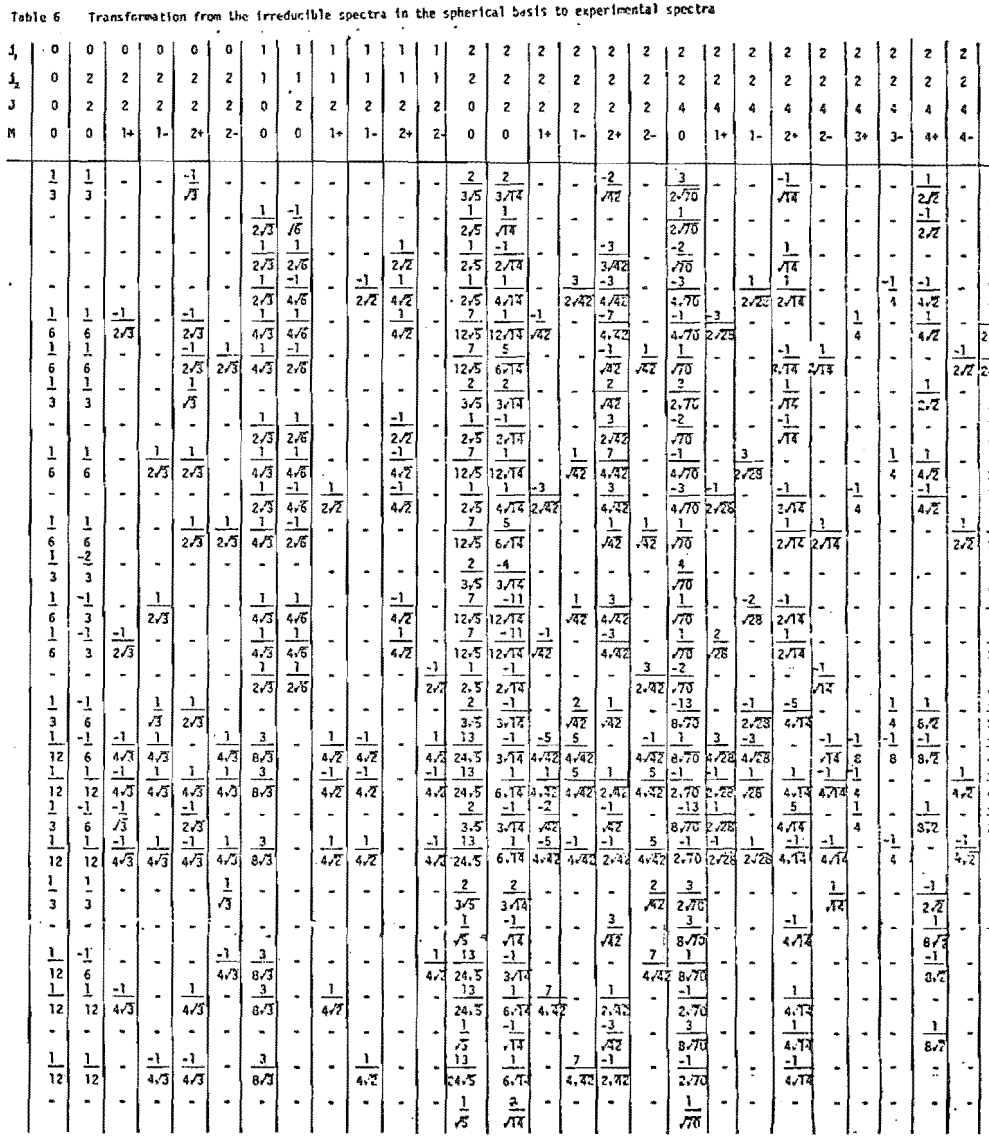

Table 5. Transformation from cartesian to experimental spectra.

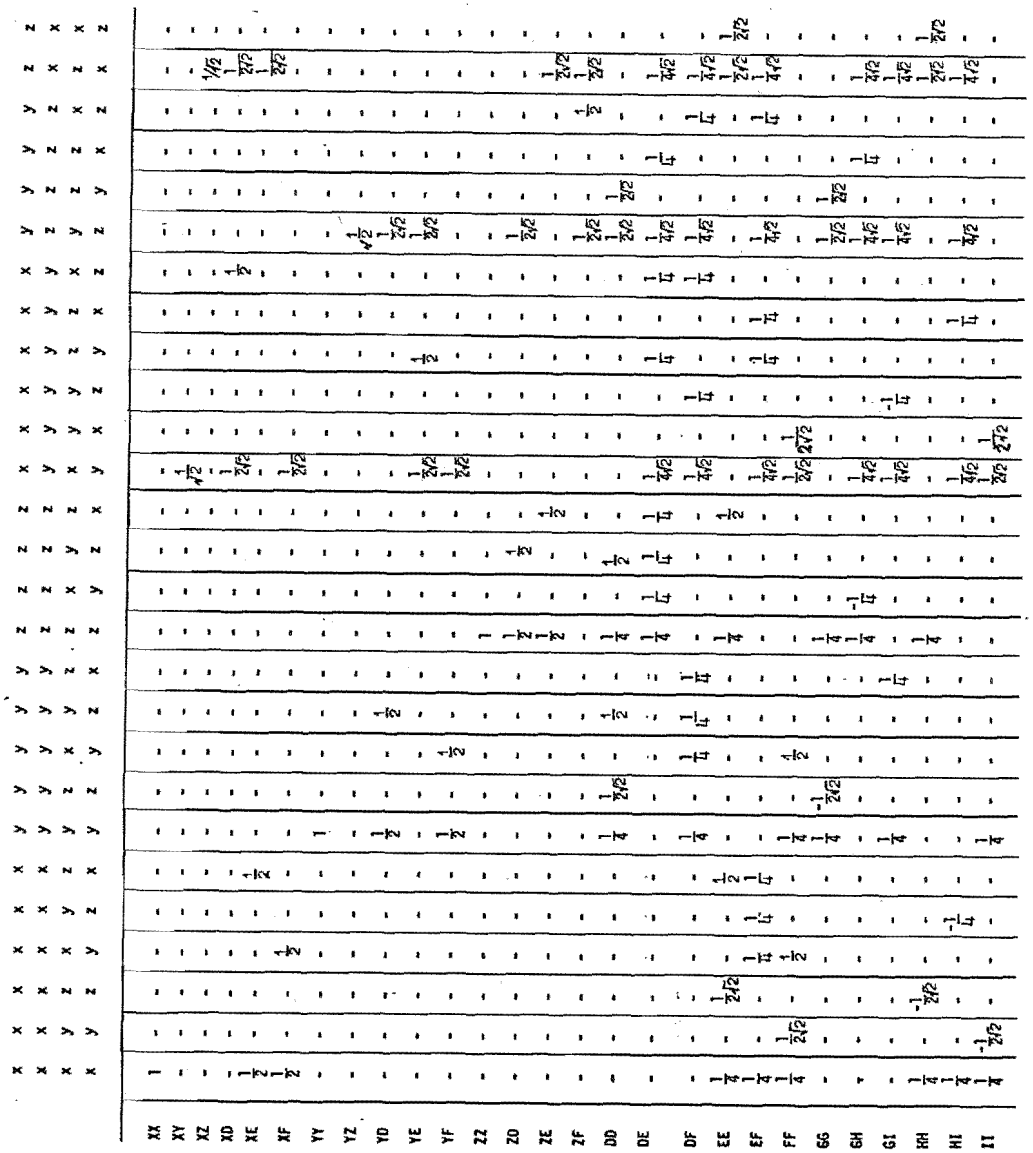

Table 6 Transformation from the irreducible spectra in the spherical basis to experimental spectra